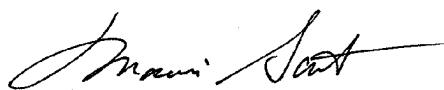


D E C L A R A T I O N

I, Masami Saito, a Japanese Patent Attorney registered No.12866, of Okabe International Patent Office at No. 602, Fuji Bldg., 2-3, Marunouchi 3-chome, Chiyoda-ku, Tokyo, Japan, hereby declare that I have a thorough knowledge of Japanese and English languages, and that the attached pages contain a correct translation into English of the priority documents of Japanese Patent Application No. 2004-174784 filed on June 11, 2004 in the name of CANON KABUSHIKI KAISHA.

I further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made, are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

signed this 4th day of August, 2008.



Masami Saito

PATENT OFFICE  
JAPANESE GOVERNMENT

This is to certify that the annexed is a true copy of the following application as filed with this Office.

Date of Application: June 11, 2004

Application Number: Japanese Patent Application  
No. 2004-174784

The country code and number  
of your priority application,  
to be used for filing abroad  
under the Paris Convention, is

Applicant(s): CANON KABUSHIKI KAISHA

June 29, 2005

Commissioner,  
Patent Office      HIROSHI OGAWA    (Seal)

2004-174784

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[Date] June 11, 2004  
[Addressed to] Commissioner, Patent Office  
[International Classification] C12N 9/24  
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[Indication of Official Fee]

[Prepayment Ledger No.] 201087

[Amount] 16000

[List of Filed Materials]

[Material]	Claims	1
[Material]	Specification	1
[Material]	Abstract	1

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**Identification No.** [000001007]

**1. Date of Change:** August 30, 1990

**(Reason of Change)** New Registration

595017850

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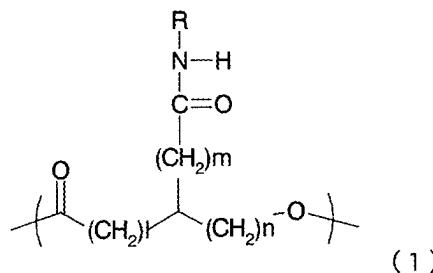
**Name:** CANON KABUSHIKI KAISHA

## [Document] CLAIMS

## [Claim 1]

A polyhydroxyalkanoate characterized in that the  
5 polyhydroxyalkanoate comprises one or more units  
represented by the chemical formula (1) in a  
molecule:

## [chemical formula 1]

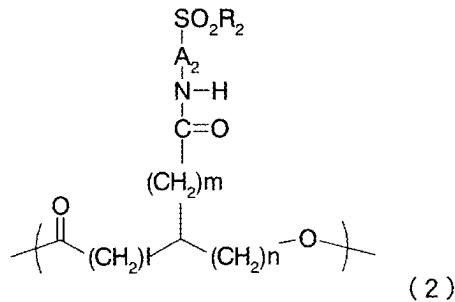


10 wherein R represents -A<sub>1</sub>-SO<sub>2</sub>R<sub>1</sub>; R<sub>1</sub> is selected from  
the group consisting of OH, a halogen atom, ONa, OK  
and OR<sub>1a</sub>; R<sub>1a</sub> and A<sub>1</sub> independently represent a group  
having a substituted or unsubstituted aliphatic  
hydrocarbon structure, a substituted or unsubstituted  
15 aromatic ring structure or a substituted or  
unsubstituted heterocyclic structure, respectively; l  
is an integer selected from 1 to 4, n is an integer  
selected from 1 to 4, and m is an integer selected  
from 0 to 8; and when two or more units are present,  
20 R, R<sub>1</sub>, R<sub>1a</sub>, A<sub>1</sub>, l, m and n mean as above independently  
for every unit.

## [Claim 2]

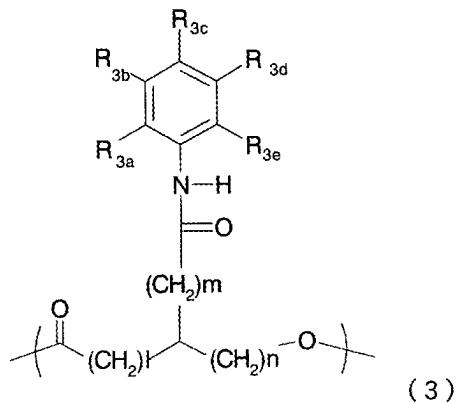
The polyhydroxyalkanoate according to claim 1 characterized in that the polyhydroxyalkanoate comprises one or more units selected from those represented by the chemical formula (2), the chemical formula (3), the chemical formula (4A) or the chemical formula (4B) in a molecule as a unit of chemical formula (1)

5 [chemical formula 2]



10 wherein R<sub>2</sub> is selected from the group consisting of OH, a halogen atom, ONa, OK and OR<sub>2a</sub>; R<sub>2a</sub> is a linear or branched alkyl group having 1 to 8 carbon atoms or a substituted or unsubstituted phenyl group; A<sub>2</sub> represents a linear or branched alkylene group having 1 to 8 carbon atoms; l is an integer selected from 1 to 4, n is an integer selected from 1 to 4 and m is an integer selected from 0 to 8; and when two or more units are present, A<sub>2</sub>, R<sub>2</sub>, R<sub>2a</sub>, l, m and n mean as above independently for every unit.

15 [chemical formula 3]



wherein  $R_{3a}$ ,  $R_{3b}$ ,  $R_{3c}$ ,  $R_{3d}$  and  $R_{3e}$  are independently  $SO_2R_{3f}$  wherein  $R_{3f}$  is selected from the group consisting of OH, a halogen atom, ONa, OK and  $OR_{3f1}$ ,

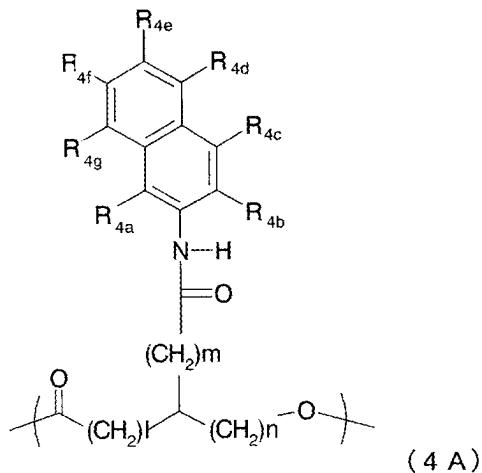
5 wherein  $OR_{3f1}$  is a linear or branched alkyl group having 1 to 8 carbon atoms or a substituted or unsubstituted phenyl group; a hydrogen atom, a halogen atom, an alkyl group having 1 to 20 carbon atoms, an alkoxy group having 1 to 20 carbon atoms,

10 OH group,  $NH_2$  group,  $NO_2$  group,  $COOR_{3g}$  group, wherein  $R_{3g}$  represents any of H atom, Na atom and K atom; an acetamide group, OPh group, NPh group,  $CF_3$  group,  $C_2F_5$  group or  $C_3F_7$  group, wherein Ph represents a phenyl group, respectively, and at least one of these

15 groups is  $SO_2R_{3f}$ ; l is an integer selected from 1 to 4, n is an integer selected from 1 to 4, and m is an integer selected from 0 to 8; and when two or more units are present,  $R_{3a}$ ,  $R_{3b}$ ,  $R_{3c}$ ,  $R_{3d}$ ,  $R_{3e}$ ,  $R_{3f}$ ,  $R_{3f1}$ ,  $R_{3g}$ , and l, m and n mean as above independently for every

20 unit

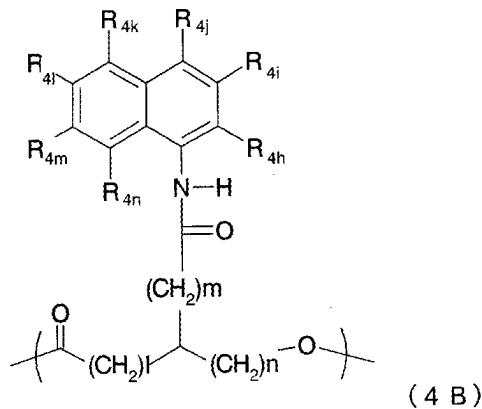
[chemical formula 4]



wherein  $R_{4a}$ ,  $R_{4b}$ ,  $R_{4c}$ ,  $R_{4d}$ ,  $R_{4e}$ ,  $R_{4f}$  and  $R_{4g}$  are independently  $SO_2R_{4o}$ , wherein  $R_{4o}$  is selected from the 5 group consisting of OH, a halogen atom, ONa, OK and  $OR_{4o1}$ , wherein  $OR_{4o1}$  is a linear or branched alkyl group having 1 to 8 carbon atoms or a substituted or unsubstituted phenyl group; a hydrogen atom, a halogen atom, an alkyl group having 1 to 20 carbon atoms, an alkoxy group having 1 to 20 carbon atoms, 10 an OH group,  $NH_2$  group,  $NO_2$  group,  $COOR_{4p}$  group, wherein  $R_{4p}$  represents any of H atom, Na atom and K atom; an acetamide group, OPh group, NPh group,  $CF_3$  group,  $C_2F_5$  group or  $C_3F_7$  group, wherein Ph represents a 15 phenyl group, respectively, and at least one of these groups is  $SO_2R_{4o}$ ; l is an integer selected from 1 to 4, n is an integer selected from 1 to 4, and m is an integer selected from 0 to 8; and when two or more

units are present, R<sub>4a</sub>, R<sub>4b</sub>, R<sub>4c</sub>, R<sub>4d</sub>, R<sub>4e</sub>, R<sub>4f</sub>, R<sub>4g</sub>, R<sub>4o</sub>, R<sub>4o1</sub>, R<sub>4p</sub>, and l, m and n mean as above independently for every unit

[chemical formula 5]



5

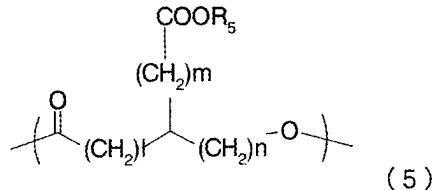
wherein R<sub>4h</sub>, R<sub>4i</sub>, R<sub>4j</sub>, R<sub>4k</sub>, R<sub>4l</sub>, R<sub>4m</sub> and R<sub>4n</sub> are independently SO<sub>2</sub>R<sub>4o</sub>, wherein R<sub>4o</sub> is selected from the group consisting of OH, a halogen atom, ONa, OK and OR<sub>4o1</sub>, wherein OR<sub>4o1</sub> is a linear or branched alkyl group having 1 to 8 carbon atoms or a substituted or unsubstituted phenyl group; a hydrogen atom, a halogen atom, an alkyl group having 1 to 20 carbon atoms, an alkoxy group having 1 to 20 carbon atoms, OH group, NH<sub>2</sub> group, NO<sub>2</sub> group, COOR<sub>4p</sub> group, wherein R<sub>4p</sub> represents any of H atom, Na atom and K atom; an acetamide group, OPh group, NHPh group, CF<sub>3</sub> group, C<sub>2</sub>F<sub>5</sub> group or C<sub>3</sub>F<sub>7</sub> group, wherein Ph represents a phenyl group, respectively, and at least one of these groups is SO<sub>2</sub>R<sub>4o</sub>; l is an integer selected from 1 to 4,

n is an integer selected from 1 to 4, and m is an integer selected from 0 to 8; and when two or more units are present, R<sub>4h</sub>, R<sub>4i</sub>, R<sub>4j</sub>, R<sub>4k</sub>, R<sub>4l</sub>, R<sub>4m</sub>, R<sub>4n</sub>, R<sub>4o</sub>, R<sub>4o1</sub>, R<sub>4p</sub>, and l, m and n mean as above independently  
5 for every unit.

[Claim 3]

A polyhydroxyalkanoate characterized in that the polyhydroxyalkanoate comprises one or more units represented by the chemical formula (5) in a  
10 molecule:

[chemical formula 6]



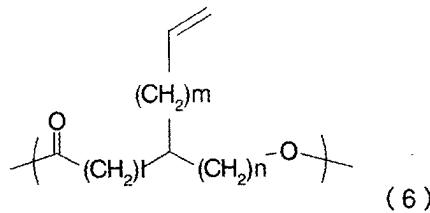
wherein R<sub>5</sub> is hydrogen, a salt forming group or R<sub>5a</sub>; R<sub>5a</sub> is a linear or branched alkyl group having 1 to  
15 12 carbon atoms, an aralkyl group or a substituent having a saccharide; l is an integer selected from 1 to 4, n is an integer selected from 1 to 4, m is an integer selected from 0 to 8; and when l is 1, 3 and 4, n is an integer selected from 1 to 4, and m is an  
20 integer selected from 0 to 8; and when l is 2 and n is 1, 3 and 4, m is an integer selected from 0 to 8; and when l is 2 and n is 2, m is an integer selected from 1 to 8; and when l is 2, n is 2 and m is 0, R<sub>5a</sub>

is a substituent having a saccharide; and when two or more units are present,  $R_5$ ,  $R_{5a}$ , and  $l$ ,  $m$  and  $n$  mean as above independently for every unit.

[Claim 4]

- 5 A polyhydroxyalkanoate characterized in that the polyhydroxyalkanoate comprises one or more units represented by the chemical formula (6) in a molecule:

[chemical formula 7]



10

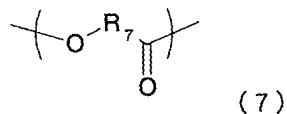
wherein  $l$  is an integer selected from 1 to 4,  $n$  is an integer selected from 1 to 4, and  $m$  is an integer selected from 0 to 8; and when two or more units are present,  $l$ ,  $m$ , and  $n$  mean as above independently for every unit.

15

[Claim 5]

- The polyhydroxyalkanoate according to any one of claims 1 to 4 characterized in that the polyhydroxyalkanoate further comprises one or more 20 units represented by the chemical formula (7) in a molecule:

[chemical formula 8]



wherein  $R_7$  is a linear or branched alkylene group having 1 to 11 carbon atoms, an alkyleneoxyalkylene group, wherein each alkylene group is independently

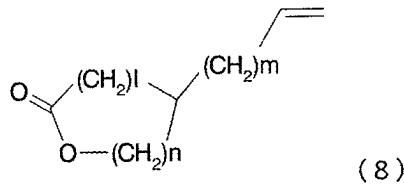
5 an alkylene group having 1 to 2 carbon atoms, respectively or an alkylidene group having 1 to 5 carbon atoms which may be substituted with aryl; and when two or more units are present,  $R_7$  means as above independently for every unit.

10 [Claim 6]

A production method of polyhydroxyalkanoate represented by the chemical formula (6) characterized in that the method comprises a step of polymerizing a compound represented by the chemical formula (8) in

15 the presence of a catalyst

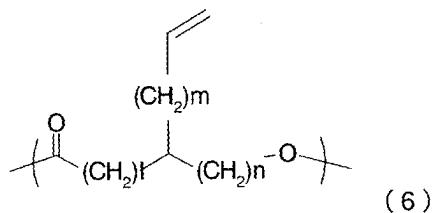
[chemical formula 9]



wherein  $l$  is an integer selected from 1 to 4,  $n$  is an integer selected from 1 to 4, and  $m$  is an integer

20 selected from 0 to 8

[chemical formula 10]

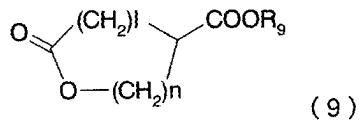


wherein l is an integer selected from 1 to 4, n is an integer selected from 1 to 4, and m is an integer  
 5 selected from 0 to 8; and when two or more units are present, l, m and n mean as above independently for every unit.

[Claim 7]

A production method of polyhydroxyalkanoate  
 10 represented by the chemical formula (10)  
 characterized in that the method comprises a step of polymerizing a compound represented by the chemical formula (9) in the presence of a catalyst

[chemical formula 11]

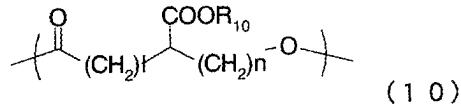


15

wherein R9 is a substituent selected from a linear or branched alkyl group having 1 to 12 carbon atoms or an aralkyl group; l is an integer selected from 1 to 4, n is an integer selected from 1 to 4, and when l

is 1, 3 or 4, n is an integer selected from 1 to 4,  
and when l is 2, n is 1, 3 or 4

[chemical formula 12]

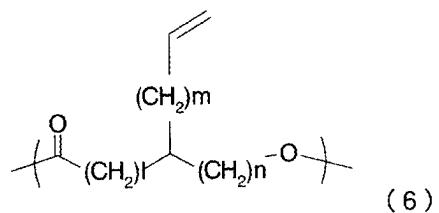


5 wherein R<sub>10</sub> is a linear or branched alkyl group  
having 1 to 12 carbon atoms or an aralkyl group; l is  
an integer selected from 1 to 4, n is an integer  
selected from 1 to 4, and when l is 1, 3 or 4, n is  
an integer selected from 1 to 4, and when l is 2, n  
10 is 1, 3 or 4; and when two or more units are present,  
l, n and R<sub>10</sub> mean as above independently for every  
unit.

[Claim 8]

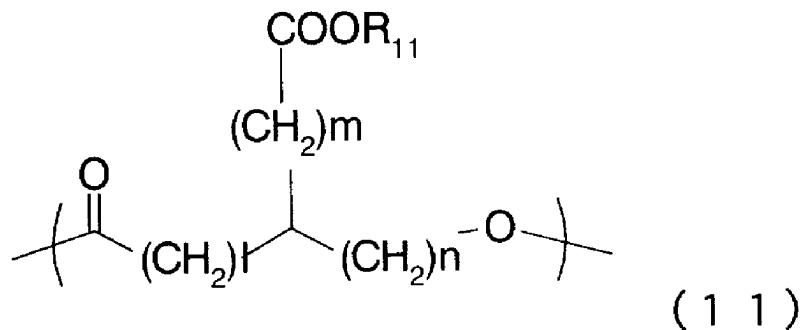
A production method of polyhydroxyalkanoate  
15 containing a unit represented by the chemical formula  
(11) characterized in that the method comprises a  
step of oxidizing a double bond portion of  
polyhydroxyalkanoate containing a unit represented by  
the chemical formula (6):

20 [chemical formula 13]



wherein l is an integer selected from 1 to 4, n is an integer selected from 1 to 4, and m is an integer selected from 0 to 8; and when two or more units are present, l, m and n mean as above independently for every unit.

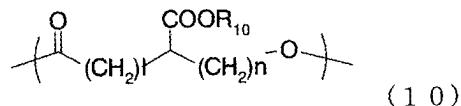
[chemical formula 14]



wherein  $R_{11}$  is hydrogen or a salt forming group; l is  
10 an integer selected from 1 to 4, n is an integer  
selected from 1 to 4, and m is an integer selected  
from 0 to 8; and when two or more units are present,  
l, m, n and  $R_{11}$  mean as above independently for every  
unit.

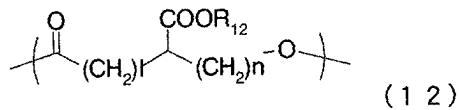
15 [Claim 9]

- A production method of polyhydroxyalkanoate containing a unit represented by the chemical formula (12) characterized in that the method comprises a step of hydrolyzing a polyhydroxyalkanoate containing 5 a unit represented by the chemical formula (10) in the presence of acid or alkali, or subjecting a polyhydroxyalkanoate containing a unit represented by the chemical formula (10) to hydrocracking including catalytic reduction:
- 10 [chemical formula 15]



wherein  $\text{R}_{10}$  is a substituent selected from a linear or branched alkyl group having 1 to 12 carbon atoms or an aralkyl group;  $\text{l}$  is an integer selected from 1 15 to 4,  $\text{n}$  is an integer selected from 1 to 4, and when  $\text{l}$  is 1, 3 or 4,  $\text{n}$  is an integer selected from 1 to 4, and when  $\text{l}$  is 2,  $\text{n}$  is 1, 3 or 4; and when two or more units are present,  $\text{l}$ ,  $\text{n}$  and  $\text{R}_{10}$  mean as above independently for every unit

20 [chemical formula 16]

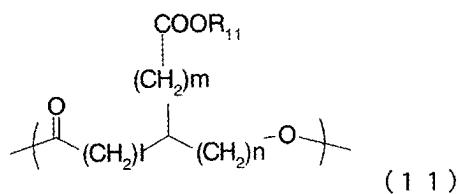


wherein R<sub>12</sub> is hydrogen or a salt forming group; l is an integer selected from 1 to 4, n is an integer selected from 1 to 4, and when l is 1, 3, and 4, n is an integer selected from 1 to 4, and when l is 2, n  
 5 is 1, 3, and 4; and when two or more units are present, l, n and R<sub>12</sub> mean as above independently for every unit.

[Claim 10]

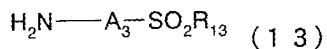
A production method of polyhydroxyalkanoate  
 10 containing a unit represented by the chemical formula  
 (1) characterized in that the method comprises a step  
 of subjecting a polyhydroxyalkanoate containing a  
 unit represented by the chemical formula (11) and at  
 least one amine compound represented by the chemical  
 15 formula (13) to condensation reaction:

[chemical formula 17]



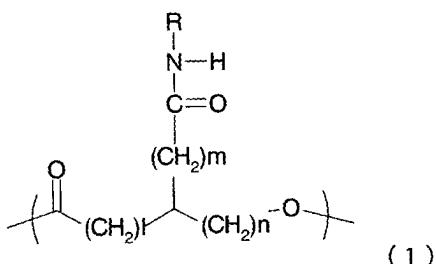
wherein R<sub>11</sub> is hydrogen or a salt forming group; l is an integer selected from 1 to 4, n is an integer  
 20 selected from 1 to 4, and m is an integer selected from 0 to 8; and when two or more units are present, l, m, n and R<sub>11</sub> mean as above independently for every unit

[chemical formula 18]



wherein  $\text{R}_{13}$  is selected from the group consisting of OH, a halogen atom, ONa, OK and OR<sub>13a</sub>; R<sub>13a</sub> and A<sub>3</sub> are  
 5 independently selected from a group having a substituted or unsubstituted aliphatic hydrocarbon structure, a substituted or unsubstituted aromatic ring structure or a substituted or unsubstituted heterocyclic structure, respectively; and when two or  
 10 more units are present, R<sub>13</sub>, R<sub>13a</sub> and A<sub>3</sub> mean as above independently for every unit

[chemical formula 19]



wherein R represents  $-\text{A}_1-\text{SO}_2\text{R}_1$ ; R<sub>1</sub> is selected from  
 15 the group consisting of OH, a halogen atom, ONa, OK and OR<sub>1a</sub>; R<sub>1a</sub> and A<sub>1</sub> independently represent a group having a substituted or unsubstituted aliphatic hydrocarbon structure, a substituted or unsubstituted aromatic ring structure or a substituted or

unsubstituted heterocyclic structure, respectively; l  
is an integer selected from 1 to 4, n is an integer  
selected from 1 to 4, and m is an integer selected  
from 0 to 8; and when two or more units are present,  
5 R, R<sub>1</sub>, R<sub>1a</sub>, A<sub>1</sub>, and l, m and n mean as above  
independently for every unit.

[Document] Specification

[Title of Invention] POLYHYDROXYALKANOATE HAVING  
VINYL GROUP, ESTER GROUP, CARBOXYL GROUP AND SULFONIC  
ACID GROUP, AND PRODUCTION METHOD THEREOF

5 [Field of the invention]

[0001]

The present invention relates to a novel polyhydroxyalkanoate and a production method thereof.

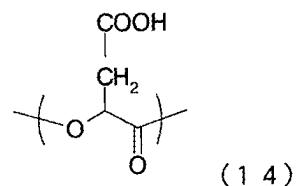
[Background of the invention]

10 [0002]

Biodegradable polymer materials are widely applied to medical materials, drug delivery systems, environmentally compatible materials, etc. In recent years, new functions besides these are further demanded and various researches have been conducted. Particularly, introducing a chemically modifiable functional group into a molecule of polyhydroxyalkanoate represented by polylactic acid is examined, and there are some reports about a compound to which a carboxyl group, a vinyl group or the like is introduced. For example, polymalic acid is known as a polyhydroxyalkanoate having a carboxyl group in the side chain. Among the polymers of this polymalic acid, there have been known  $\alpha$ -type compounds represented by the chemical formula (14):

[0003]

[chemical formula 1]

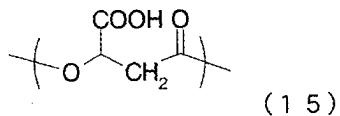


[0004]

and  $\beta$ -type compounds represented by the chemical formula (15) :

5 [0005]

[chemical formula 2]



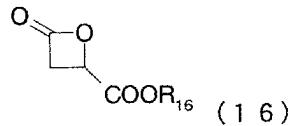
[0006]

which are different in the way of polymer formation.

10 Among these, as for the  $\beta$ -type polymalic acid and its copolymer, a polymer obtained by ring-opening polymerization of benzyl ester of  $\beta$ -malolactone represented by the chemical formula (16) :

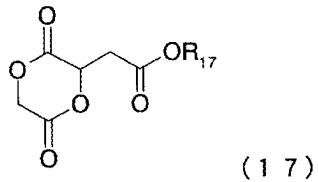
[0007]

15 [chemical formula 3]



[0008]

- (R<sub>16</sub>: benzyl group) is disclosed in the specification of U.S. Patent No. 4265247 (Patent Document 1). In addition, as for the  $\alpha$ -type polymalic acid-glycolic acid copolymer and other copolymers containing
- 5 hydroxyalkanoic acid including glycolic acid, polymers obtained by copolymerizing a 6-membered cyclic diester monomer represented by the chemical formula (17):
- [0009]
- 10 [chemical formula 4]



- [0010]
- wherein R<sub>17</sub> represents a lower alkyl group such as a methyl group, an ethyl group, n-propyl group, an isopropyl group, and a t-butyl group and a benzyl group, etc., and a glycolide and lactide which are cyclic diesters, a lactone which is an ester by intramolecular ring closure reaction of  $\omega$ -hydroxycarboxylic acid are disclosed in Japanese
- 15 Patent Application Laid-Open No. H2-3415 (Patent Document 2).
- 20

[0011]

In addition, with regard to a polyhydroxyalkanoate

having a carboxyl group on a side chain, it is disclosed in Macromolecules 2000, 33 (13), 4619-4627 (Nonpatent Document 1) that ring-opening polymerization of 7-oxo-4-oxepane carboxylate ester 5 is conducted to prepare a polymer having an ester group on a side chain, which is further subjected to hydrocracking to prepare a polymer having carboxylic acid on a side chain. Biomacromolecules 2000, 1, 275 (Nonpatent Document 2) discloses a polymer to which 10 benzyloxycarbonyl group is introduced at the  $\alpha$ -position methylene group of a carbonyl group in the poly( $\epsilon$ -caprolactone) main chain by reacting poly( $\epsilon$ -caprolactone) with lithium diisopropylamide and further reacting with benzyl chloroformate.

15 Macromolecular Bioscience 2004, 4, 232 (Nonpatent Document 3) discloses a polymer to which (benzyloxycarbonyl)methyl group is introduced at the  $\alpha$ -position methylene group of a carbonyl group in the polylactic acid main chain by reacting polylactic acid with lithium diisopropyl amide and further 20 reacting with benzyl bromoacetate.

With regard to a polyhydroxyalkanoate having a vinyl group on a side chain, Polymeric Materials Science & Engineering 2002, 87, 254 (Nonpatent Document 4) discloses a polymer obtained by ring-opening polymerization of  $\alpha$ -allyl( $\delta$ -valerolactone). With regard to a polyhydroxyalkanoate having a vinyl

group on a side chain, Polymer Preprints 2002, 43 (2),  
727 (Nonpatent Document 5) also discloses a polymer  
obtained by ring-opening polymerization of 3,6-  
diallyl-1,4-dioxane-2,5-dione which is a 6-membered  
5 ring diester monomer.

[0012]

As mentioned above, there have been reported  
polymers having new functions imparted by further  
introducing a functionality providing structure to a  
10 polyhydroxyalkanoate to which a chemically modifiable  
functional group has been introduced. In  
International Journal of Biological Macromolecules 25  
(1999) 265 (Nonpatent Document 6), ring-opening  
polymerization of a cyclic dimer of  $\alpha$ -malic acid and  
15 glycolic acid gives a copolymer of  $\alpha$ -type malic acid  
and glycolic acid, and a polyester having a carboxyl  
group on a side chain is obtained by deprotecting the  
obtained polymer. It is described that carboxyl group  
of a side chain of this compound was subjected to  
20 chemical modification with a tripeptide, the obtained  
polymer was evaluated about cellular adhesiveness and  
good results were obtained.

[Patent Document 1] U.S. Patent No. 4265247

[Patent Document 2] Japanese Patent Application Laid-  
25 Open No. H2-3415

[Nonpatent Document 1] Macromolecules 2000, 33 (13),  
4619-4627

[Nonpatent Document 2] Biomacromolecules 2000, 1, 275  
[Nonpatent Document 3] Macromolecular Bioscience 2004,  
4, 232  
[Nonpatent Document 4] Polymeric Materials Science &  
5 Engineering 2002, 87, 254  
[Nonpatent Document 5] Polymer Preprints 2002, 43 (2),  
727  
[Nonpatent Document 6] International Journal of  
Biological Macromolecules 25 (1999) 265  
10  
[Disclosure of the invention]  
[Problem(s) to be Solved by the Invention]  
[0013]  
Although it is supposed to be possible to  
15 impart a new functionality by introducing a unit  
having a carboxyl group or a unit having a vinyl  
group which are reactive functional groups into a  
molecule and carrying out chemical modification of  
the reactive functional group as mentioned above,  
20 there have been few reports. Accordingly, the  
present invention provides a new polyhydroxyalkanoate  
having a reactive functional group in a molecule and  
a new polyhydroxyalkanoate having a new function  
imparted by performing chemical modification of the  
25 polyhydroxyalkanoate having a reactive functional  
group and a production method thereof.  
[Means for Solving the Problem]

[0014]

Therefore, the present inventors have conducted intensive studies aiming at developing a new polyhydroxyalkanoate having a reactive functional group in a molecule and a new polyhydroxyalkanoate having a new function imparted by performing chemical modification of the polyhydroxyalkanoate having a reactive functional group and consequently achieved 5 the invention shown below.

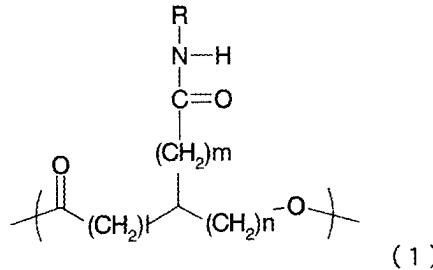
10 [0015]

Polyhydroxyalkanoates according to the present invention include the following.

(1) A polyhydroxyalkanoate comprising one or more units represented by the chemical formula (1) in a 15 molecule:

[0016]

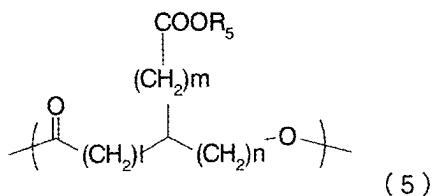
[chemical formula 5]



[0017]

20 wherein R represents  $-\text{A}_1-\text{SO}_2\text{R}_1$ ;  $\text{R}_1$  is selected from the group consisting of OH, a halogen atom, ONa, OK and OR<sub>1a</sub>; R<sub>1a</sub> and A<sub>1</sub> independently represent a group

- having a substituted or unsubstituted aliphatic hydrocarbon structure, a substituted or unsubstituted aromatic ring structure or a substituted or unsubstituted heterocyclic structure, respectively; l 5 is an integer selected from 1 to 4, n is an integer selected from 1 to 4, and m is an integer selected from 0 to 8; and when two or more units are present, R, R<sub>1</sub>, R<sub>1a</sub>, A<sub>1</sub>, and l, m and n mean as above independently for every unit.
- 10 (2) A polyhydroxyalkanoate comprising one or more units represented by the chemical formula (5) in a molecule:
- [0018]
- [chemical formula 6]



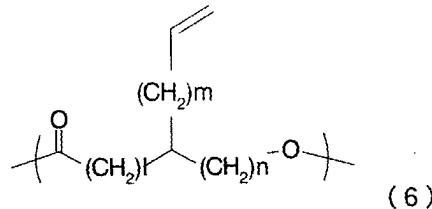
- 15
- [0019]
- wherein R<sub>5</sub> is hydrogen, a salt forming group or R<sub>5a</sub>; R<sub>5a</sub> is a linear or branched alkyl group having 1 to 12 carbon atoms, an aralkyl group or a substituent 20 having a saccharide; l is an integer selected from 1 to 4, n is an integer selected from 1 to 4, m is an integer selected from 0 to 8; and when l is 1, 3 and 4, n is an integer selected from 1 to 4, and m is an

integer selected from 0 to 8; and when l is 2 and n is 1, 3 and 4, m is an integer selected from 0 to 8; and when l is 2 and n is 2, m is an integer selected from 1 to 8; and when l is 2, n is 2 and m is 0, R<sub>5a</sub> 5 is a substituting group having a saccharide; and when two or more units are present, R<sub>5</sub>, R<sub>5a</sub>, and l, m and n mean as above independently for every unit.

(3) A polyhydroxyalkanoate comprising one or more units represented by the chemical formula (6) in a 10 molecule:

[0020]

[chemical formula 7]



[0021]

15 wherein l is an integer selected from 1 to 4, n is an integer selected from 1 to 4, and m is an integer selected from 0 to 8; and when two or more units are present, l, m, and n mean as above independently for every unit.

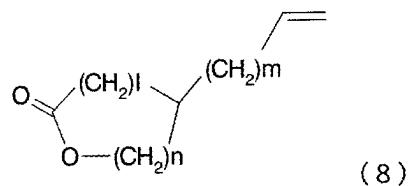
20 On the other hand, the production method of polyhydroxyalkanoate according to the present invention includes the following.

(A) A production method of polyhydroxyalkanoate

represented by the chemical formula (6) having a step of polymerizing a compound having a unit represented by the chemical formula (8) in the presence of a catalyst.

5 [0022]

[chemical formula 8]

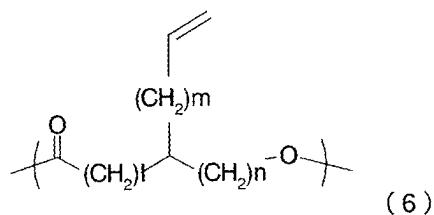


[0023]

wherein l is an integer selected from 1 to 4, n is an  
10 integer selected from 1 to 4, and m is an integer  
selected from 0 to 8.

[0024]

[chemical formula 9]



15 [0025]

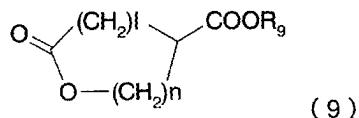
wherein l is an integer selected from 1 to 4, n is an integer selected from 1 to 4, and m is an integer selected from 0 to 8; and when two or more units are

present, l, m and n mean as above independently for every unit.

(B) A production method of polyhydroxyalkanoate represented by the chemical formula (10) having a 5 step of polymerizing a compound represented by the chemical formula (9) in the presence of a catalyst.

[0026]

[chemical formula 10]

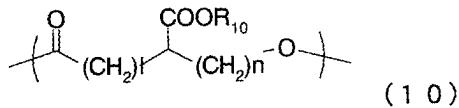


10 [0027]

wherein  $R_9$  is a substituent selected from a linear or branched alkyl group having 1 to 12 carbon atoms or an aralkyl group; l is an integer selected from 1 to 4, n is an integer selected from 1 to 4, and when l 15 is 1, 3 or 4, n is an integer selected from 1 to 4, and when l is 2, n is 1, 3 or 4.)

[0028]

[chemical formula 11]



20 [0029]

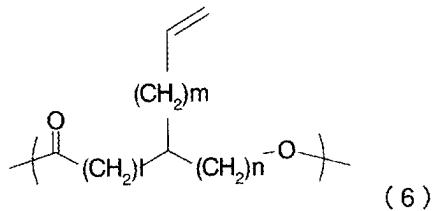
wherein  $R_{10}$  is a substituent selected from a linear

or branched alkyl group having 1 to 12 carbon atoms or an aralkyl group; l is an integer selected from 1 to 4, n is an integer selected from 1 to 4, and when l is 1, 3 or 4, n is an integer selected from 1 to 4, 5 and when l is 2, n is 1, 3 or 4; and when two or more units are present, l, n and R<sub>10</sub> mean as above independently for every unit.

(C) A production method of polyhydroxyalkanoate containing a unit represented by the chemical formula 10 (11) having a step of oxidizing a double bond portion of polyhydroxyalkanoate containing a unit represented by the chemical formula (6):

[0030]

[chemical formula 12]



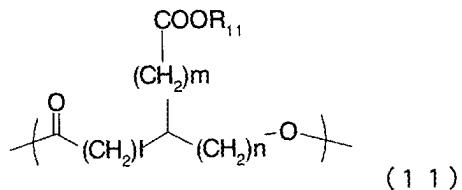
15

[0031]

wherein l is an integer selected from 1 to 4, n is an integer selected from 1 to 4, and m is an integer selected from 0 to 8; and when two or more units are 20 present, l, m and n mean as above independently for every unit.

[0032]

[chemical formula 13]



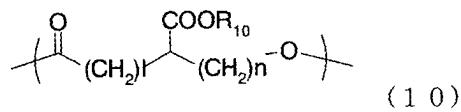
[0033]

wherein R<sub>11</sub> is hydrogen or a salt forming group; l is an integer selected from 1 to 4, n is an integer  
5 selected from 1 to 4, and m is an integer selected from 0 to 8; and when two or more units are present, l, m, n and R<sub>11</sub> mean as above independently for every unit.

(D) A production method of polyhydroxyalkanoate  
10 containing a unit represented by the chemical formula  
(12) having a step of hydrolyzing a  
polyhydroxyalkanoate containing a unit represented by  
the chemical formula (10) in the presence of acid or  
alkali, or subjecting a polyhydroxyalkanoate  
15 containing a unit represented by the chemical formula  
(10) to hydrocracking including catalytic reduction:

[0034]

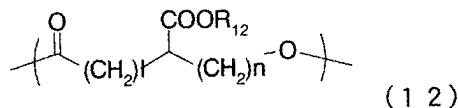
[chemical formula 14]



20 [0035]

wherein  $R_{10}$  is a substituent selected from a linear or branched alkyl group having 1 to 12 carbon atoms or an aralkyl group; l is an integer selected from 1 to 4, n is an integer selected from 1 to 4, and when 5 l is 1, 3 or 4, n is an integer selected from 1 to 4, and when l is 2, n is 1, 3 or 4; and when two or more units are present, l, n and  $R_{10}$  mean as above independently for every unit.

[0036]  
10 [chemical formula 15]

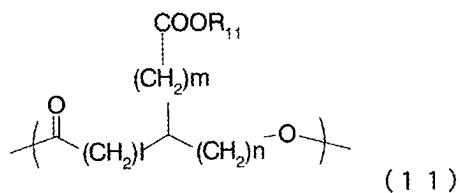


[0037]  
wherein  $R_{12}$  is hydrogen or a salt forming group; l is an integer selected from 1 to 4, n is an integer 15 selected from 1 to 4, and when l is 1, 3, and 4, n is an integer selected from 1 to 4, and when l is 2, n is 1, 3, and 4; and when two or more units are present, l, n and  $R_{12}$  mean as above independently for every unit.  
20 (E) A production method of polyhydroxyalkanoate containing a unit represented by the chemical formula (1) having a step of subjecting a polyhydroxyalkanoate containing a unit represented by the chemical formula (11) and at least one amine

compound represented by the chemical formula (13) to condensation reaction:

[0038]

[chemical formula 16]



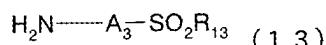
5

[ 0039 ]

wherein  $R_{11}$  is hydrogen or a salt forming group; l is an integer selected from 1 to 4, n is an integer selected from 1 to 4, and m is an integer selected from 0 to 8; and when two or more units are present, l, m, n and  $R_{11}$  mean as above independently for every unit.

[00401]

[chemical formula 17]



15

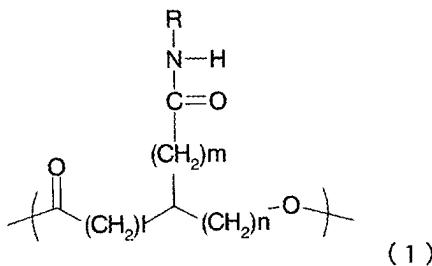
[0041]

wherein R<sub>13</sub> is selected from the group consisting of OH, a halogen atom, ONa, OK and OR<sub>13a</sub>; R<sub>13a</sub> and A<sub>3</sub> are independently selected from a group having a substituted or unsubstituted aliphatic hydrocarbon structure, a substituted or unsubstituted aromatic

ring structure or a substituted or unsubstituted heterocyclic structure, respectively; and when two or more units are present,  $R_{13}$ ,  $R_{13a}$  and  $A_3$  mean as above independently for every unit.

5 [0042]

[chemical formula 18]



[0043]

wherein  $R$  represents  $-A_1-SO_2R_1$ ;  $R_1$  is selected from  
 10 the group consisting of OH, a halogen atom, ONa, OK  
 and OR<sub>1a</sub>;  $R_{1a}$  and  $A_1$  independently represent a group  
 having a substituted or unsubstituted aliphatic  
 hydrocarbon structure, a substituted or unsubstituted  
 aromatic ring structure or a substituted or  
 15 unsubstituted heterocyclic structure, respectively;  $l$   
 is an integer selected from 1 to 4,  $n$  is an integer  
 selected from 1 to 4, and  $m$  is an integer selected  
 from 0 to 8; and when two or more units are present,  
 20  $R$ ,  $R_1$ ,  $R_{1a}$ ,  $A_1$ ,  $l$ ,  $m$  and  $n$  mean as above independently  
 for every unit.

[Best Mode of Carrying Out the Invention]

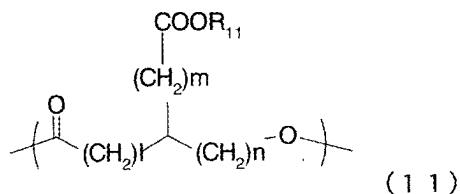
[0044]

Hereinbelow, the present invention is described in more detail referring to preferable embodiments.

The target polyhydroxyalkanoate represented by the  
 5 chemical formula (1) in the present invention can be prepared by reacting polyhydroxyalkanoate containing a unit represented by the chemical formula (11) used as a starting material and at least one aminosulfonic acid compound represented by the chemical formula  
 10 (13).

[0045]

[chemical formula 19]

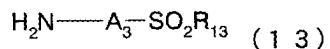


[0046]

15 wherein R<sub>11</sub> is hydrogen or a salt forming group; l is an integer selected from 1 to 4, n is an integer selected from 1 to 4, and m is an integer selected from 0 to 8; and when two or more units are present,  
 20 l, m, n and R<sub>11</sub> mean as above independently for every unit.

[0047]

[chemical formula 20]



[0048]

wherein  $\text{R}_{13}$  is selected from the group consisting of OH, a halogen atom, ONa, OK and OR<sub>13a</sub>; R<sub>13a</sub> and A<sub>3</sub> are independently selected from a group having a substituted or unsubstituted aliphatic hydrocarbon structure, a substituted or unsubstituted aromatic ring structure or a substituted or unsubstituted heterocyclic structure, respectively (here, R<sub>13a</sub> is a monovalent group having a structure selected from these and A<sub>3</sub> is a divalent group having a structure selected from these); and when two or more units are present, R<sub>13</sub>, R<sub>13a</sub> and A<sub>3</sub> mean as above independently for every unit.

More in detail, R<sub>13</sub> is selected from the group consisting of OH, a halogen atom, ONa, OK and OR<sub>13a</sub>. R<sub>13a</sub> is a linear or branched alkyl group having 1 to 8 carbon atoms or a substituted or unsubstituted phenyl group. A<sub>3</sub> represents a group having a linear or branched substituted or unsubstituted C<sub>1</sub> to C<sub>8</sub> alkylene group, a substituted or unsubstituted phenylene group, a substituted or unsubstituted naphthalene group or a substituted or unsubstituted group having a heterocyclic structure containing one or more N, S and O. When A<sub>3</sub> is a cyclic structure,

(a) unsubstituted ring(s) may be further condensed.

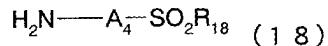
Further, when two or more units are present, R<sub>13</sub>, R<sub>13a</sub> and A<sub>3</sub> mean as above independently for every unit.

[0049]

5 In the case that A<sub>3</sub> is a linear and substituted or unsubstituted alkylene group, aminosulfonic acid compounds represented by the following chemical formula (18) can be mentioned.

[0050]

10 [chemical formula 21]



[0051]

wherein R<sub>18</sub> is selected from the group consisting of OH, a halogen atom, ONa, OK and OR<sub>18a</sub>; R<sub>18a</sub> is a linear or branched alkyl group having 1 to 8 carbon atoms or 15 a substituted or unsubstituted phenyl group; A<sub>4</sub> is a linear or branched substituted or unsubstituted C<sub>1</sub> to C<sub>8</sub> alkylene group and when it is substituted, it may be substituted with an alkyl group having 1 to 20 carbon atoms, an alkoxy group having 1 to 20 carbon atoms, etc.

As a compound represented by the chemical formula (18), 2-aminoethanesulfonic acid (taurine), 3-aminopropanesulfonic acid, 4-aminobutanesulfonic acid, 2-amino-2-methylpropanesulfonic acid, and

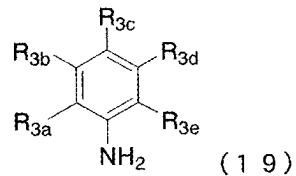
alkaline metal salts and ester compounds thereof, etc.  
can be mentioned.

[0052]

In the case that A<sub>3</sub> is a substituted or  
5 unsubstituted phenylene group, aminosulfonic acid  
compounds represented by the following chemical  
formula (19) can be mentioned.

[0053]

[chemical formula 22]



10

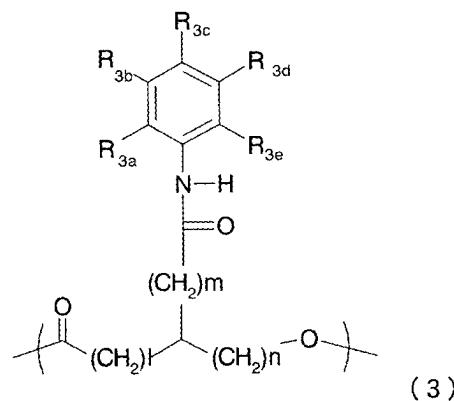
[0054]

wherein R<sub>3a</sub>, R<sub>3b</sub>, R<sub>3c</sub>, R<sub>3d</sub> and R<sub>3e</sub> are independently  
selected from the group consisting of SO<sub>2</sub>R<sub>3f</sub>, wherein  
R<sub>3f</sub> is selected from the group consisting of OH, a  
15 halogen atom, ONa, OK and OR<sub>3f1</sub> wherein OR<sub>3f1</sub> is a  
linear or branched alkyl group having 1 to 8 carbon  
atoms or a substituted or unsubstituted phenyl group,  
a hydrogen atom, a halogen atom, an alkyl group  
having 1 to 20 carbon atoms, an alkoxy group having 1  
20 to 20 carbon atoms, OH group and NH<sub>2</sub> group and NO<sub>2</sub>  
group, COOR<sub>3g</sub>, wherein R<sub>3g</sub> represents any of H atom,  
Na atom and K atom, an acetamide group, OPh group,  
NHPH group, CF<sub>3</sub> group, C<sub>2</sub>F<sub>5</sub> or C<sub>3</sub>F<sub>7</sub> group,

respectively, wherein Ph represents a phenyl group,  
and at least one of the groups of these is  $\text{SO}_2\text{R}_{3f}$ ; and  
when two or more units are present,  $\text{R}_{3a}$ ,  $\text{R}_{3b}$ ,  $\text{R}_{3c}$ ,  $\text{R}_{3d}$ ,  
 $\text{R}_{3e}$ ,  $\text{R}_{3f}$ ,  $\text{R}_{3f1}$  and  $\text{R}_{3g}$  mean as above independently for  
5 every unit.

By using the compound represented by the  
chemical formula (19), polyhydroxyalkanoate which  
contains in a molecule one or more units represented  
by the chemical formula (3) can be obtained.  
10 [0055]

[chemical formula 23]



[0056]  
wherein  $\text{R}_{3a}$ ,  $\text{R}_{3b}$ ,  $\text{R}_{3c}$ ,  $\text{R}_{3d}$ ,  $\text{R}_{3e}$ , and l, n and m are  
15 similarly defined as the above.

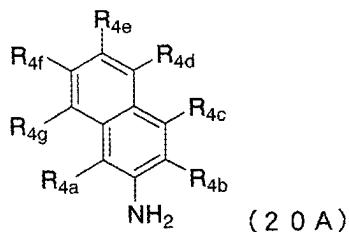
As a compound represented by the chemical  
formula (19), p-aminobenzenesulfonic acid (sulfanilic  
acid), m-aminobenzenesulfonic acid, o-  
aminobenzenesulfonic acid, m-toluidine-4-sulfonic  
20 acid, o-toluidine-4-sulfonic acid sodium salt, p-

toluidine-2-sulfonic acid, 4-methoxyaniline-2-sulfonic acid, o-anisidine-5-sulfonic acid, p-anisidine-3-sulfonic acid, 3-nitroaniline-4-sulfonic acid, 2-nitroaniline-4-sulfonic acid sodium salt, 4-5 nitroaniline-2-sulfonic acid sodium salt, 1,5-dinitroaniline-4-sulfonic acid, 2-aminophenol-4-hydroxy-5-nitrobenzenesulfonic acid, 2,4-dimethylaniline-5-sulfonic acid sodium salt, 2,4-dimethylaniline-6-sulfonic acid, 3,4-dimethylaniline-10 5-sulfonic acid, 4-isopropylaniline-6-sulfonic acid, 4-trifluoromethylaniline-6-sulfonic acid, 3-carboxy-4-hydroxyaniline-5-sulfonic acid, 4-carboxyaniline-6-sulfonic acid and alkaline metal salts and ester compounds thereof, etc. can be mentioned.

15 [0057]

In the case that  $A_3$  is a substituted or unsubstituted napthalene group, aminosulfonic acid compounds represented by the following chemical formula (20A) or (20B) can be mentioned.

20 [0058]  
[chemical formula 24]

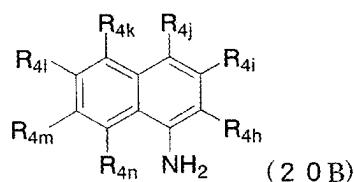


[0059]

wherein  $R_{4a}$ ,  $R_{4b}$ ,  $R_{4c}$ ,  $R_{4d}$ ,  $R_{4e}$ ,  $R_{4f}$  and  $R_{4g}$  are independently  $SO_2R_{4o}$ , wherein  $R_{4o}$  is selected from the group consisting of OH, a halogen atom, ONa, OK and  $OR_{4o1}$ , wherein  $OR_{4o1}$  is a linear or branched alkyl group having 1 to 8 carbon atoms or a substituted or unsubstituted phenyl group; a hydrogen atom, a halogen atom, an alkyl group having 1 to 20 carbon atoms, an alkoxy group having 1 to 20 carbon atoms, OH group,  $NH_2$  group,  $NO_2$  group,  $COOR_{4p}$  group, wherein 5  $R_{4p}$  represents any of H atom, Na atom and K atom; an acetamide group, OPh group, NPh group,  $CF_3$  group,  $C_2F_5$  group or  $C_3F_7$  group, wherein Ph represents a phenyl group, respectively, and at least one of these 10 groups is  $SO_2R_{4o}$ .

15 [0060]

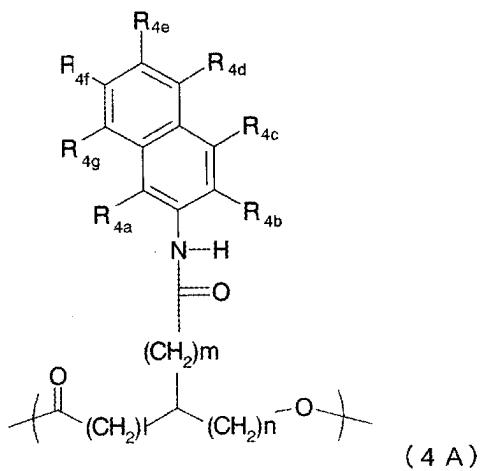
[chemical formula 25]



[0061]

wherein  $R_{4h}$ ,  $R_{4i}$ ,  $R_{4j}$ ,  $R_{4k}$ ,  $R_{4l}$ ,  $R_{4m}$  and  $R_{4n}$  are independently  $SO_2R_{4o}$  wherein  $R_{4o}$  is selected from the group consisting of OH, a halogen atom, ONa, OK and  $OR_{4o1}$ , wherein  $R_{4o1}$  is a linear or branched alkyl group having 1 to 8 carbon atoms or a substituted or 20

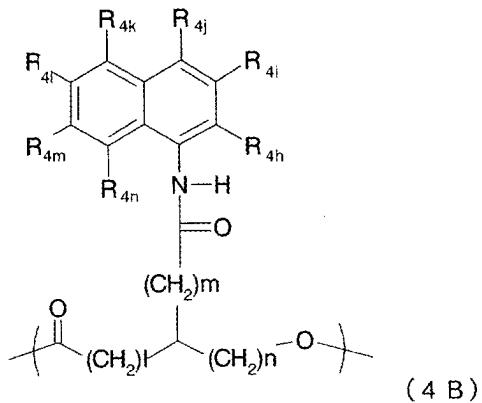
- unsubstituted phenyl group; a hydrogen atom, a halogen atom, an alkyl group having 1 to 20 carbon atoms, an alkoxy group having 1 to 20 carbon atoms, OH group, NH<sub>2</sub> group, NO<sub>2</sub> group, COOR<sub>4p</sub> group, wherein
- 5 R<sub>4p</sub> represents any of H atom, Na atom and K atom; an acetamide group, OPh group, NHPH group, CF<sub>3</sub> group, C<sub>2</sub>F<sub>5</sub> group or C<sub>3</sub>F<sub>7</sub> group, wherein Ph represents a phenyl group, respectively, and at least one of these groups is SO<sub>2</sub>R<sub>4o</sub>.
- 10 Polyhydroxyalkanoate which contains one or more units represented by the chemical formula (4A) or (4B) in a molecule can be obtained by using a compound represented by the chemical formula (20A) or (20B).
- 15 [0062]  
 [chemical formula 26]



[0063]

wherein  $R_{4a}$ ,  $R_{4b}$ ,  $R_{4c}$ ,  $R_{4d}$ ,  $R_{4e}$ ,  $R_{4f}$  and  $R_{4g}$  and  $l$ ,  $n$  and  $m$  are defined same as above.

[chemical formula 27]



5 [0064]

wherein  $R_{4h}$ ,  $R_{4i}$ ,  $R_{4j}$ ,  $R_{4k}$ ,  $R_{4l}$ ,  $R_{4m}$  and  $R_{4n}$  and  $l$ ,  $n$  and  $m$  are defined same as above.

As a compound represented by the chemical formula (20A) or (20B), 1-naphthylamine 5-sulfonic acid, 1-naphthylamine 4-sulfonic acid, 1-naphthylamine 8-sulfonic acid, 2-naphthylamine 5-sulfonic acid, 1-naphthylamine 6-sulfonic acid, 1-naphthylamine-7-sulfonic acid, 1-naphthylamine-2-ethoxy-6-sulfonic acid, 1-amino-2-naphthol-4-sulfonic acid, 6-amino-1-naphthol-3-sulfonic acid, 1-amino-8-naphthol-2,4-sulfonic acid monosodium salt, 1-amino-8-naphthol-3,6-disulfonic acid monosodium salt, and alkaline metal salts and ester compounds thereof, etc. can be mentioned.

20 [0065]

In the case that  $A_3$  is a substituted or unsubstituted group having a heterocyclic structure containing one or more N, S and O, the heterocyclic structure may be any one of pyridine ring, a 5 piperazine ring, a furan ring, a thiol ring, etc. As a compound, sulfonic acid such as 2-aminopyridine-6-sulfonic acid and 2-aminopiperazine-6-sulfonic acid and alkaline metal salts and ester compounds thereof, etc. can be mentioned.

10 As a group which binds to a sulfonic acid through an ester bond in the case of sulfonic ester, a group having a substituted or unsubstituted aliphatic hydrocarbon structure, a substituted or unsubstituted aromatic ring structure or a 15 substituted or unsubstituted heterocyclic structure can be mentioned as above. Furthermore, a linear or branched alkyl group having 1 to 8 carbon atoms, a substituted or unsubstituted phenyl group is preferable. From the viewpoints such as readiness of 20 esterification,  $OCH_3$ ,  $OC_2H_5$ ,  $OC_6H_5$ ,  $OC_3H_7$ ,  $OC_4H_9$ ,  $OCH(CH_3)_2$ ,  $OCH_2CH_3)_3$ ,  $OC(CH_3)_3$ , etc. are more preferable.

[0066]

(Production method of polyhydroxyalkanoate having a 25 unit represented by the chemical formula (1))

A reaction of polyhydroxyalkanoate containing a unit represented by the chemical formula (11) with an

aminosulfonic acid compound represented by the chemical formula (13) in the present invention is described in detail.

[0067]

5       The amount of the compound represented by the chemical formula (13) used in the present invention is in the range of 0.1 to 50.0 times in mol, preferably 1.0 to 20.0 times in mol for a unit represented by the chemical formula (11) used as a  
10 starting material.

[0068]

There is a condensation reaction by thermal dehydration etc. as a method of generating an amide bond from the carboxylic acid and amine of the  
15 present invention. Particularly, a method of activating a carboxylic acid moiety by an activating agent to generate an active acyl intermediate and then reacting it with an amine is effective from the viewpoint of such mild reaction conditions so that  
20 ester bonds in the polymer main chain may not be cleaved. As an active acyl intermediate, an acid halide, an acid anhydride, active ester, etc. can be mentioned. Particularly, a method of using condensing agent and forming an amide bond all over  
25 the same reaction space is preferable from the viewpoint of simplification of productive process. If necessary, it is also possible to perform a

condensation reaction with an amine after isolating as an acid halide.

[0069]

As a usable condensing agent, a phosphate condensing agent used for polycondensation of aromatic polyamide, a carbodiimide condensing agent used for peptide synthesis, an acid chloride condensing agent, etc. can be suitably selected based on the combination of the compounds of chemical formulas (13) and (11).

[0070]

As the phosphate condensing agent, a phosphorous acid ester condensing agent, a phosphorus chloride condensing agent, a phosphoric acid anhydride condensing agent, a phosphoric acid ester condensing agent, a phosphoric acid amide condensing agent, etc. can be mentioned.

It is possible to use a condensing agent such as a phosphorous acid ester in the reaction of the present invention. Examples of phosphorous acid ester used on this occasion include triphenyl phosphite, diphenyl phosphite, tri-o-tolyl phosphite, di-o-tolyl phosphite, tri-m-tolyl phosphite, di-m-tolyl phosphite, tri-p-tolyl phosphite, di-p-tolyl phosphite, di-o-chlorophenyl phosphite, tri-p-chlorophenyl phosphite, di-p-chlorophenyl phosphite, trimethyl phosphite, triethyl phosphite, etc.

Particularly, triphenyl phosphite is used preferably. A metal salt such as lithium chloride and calcium chloride may be also added for the improvement of properties such as solubility of and reactivity the 5 polymer.

[0071]

As the carbodiimide condensing agent, dicyclohexylcarbodiimide (DCC), N-ethyl-N'-3-dimethylaminopropylcarbodiimide (EDC=WSCl), 10 diisopropylcarbodiimide (DIPC), etc. can be mentioned. N-hydroxysuccinimide (HONSu), 1-hydroxybenzotriazole (HOBr) or 3-hydroxy-4-oxo-3,4-dihydro-1,2,3-benzotriazine (HOObt), etc. may be used in combination with DCC or WSCl.

15 [0072]

The amount of the condensing agent used is in the range of 0.1 to 50 times in mol, preferably 1.0 to 20 times in mol for a unit represented by the chemical formula (11).

20 [0073]

A solvent can be used, if needed, in the reaction of the present invention. The solvents to be used include hydrocarbons such as hexane, cyclohexane and heptane, ketones such as acetone and 25 methyl ethyl ketone, ethers such as dimethyl ether, diethyl ether, tetrahydrofuran, halogenated hydrocarbons such as dichloromethane, chloroform,

carbon tetrachloride, dichloroethane and trichloroethane, aromatic hydrocarbons such as benzene and toluene, aprotic polar solvents such as N,N-dimethylformamide, dimethylsulfoxide,  
5 dimethylacetamide, and hexamethylphosphoramide, pyridine, pyridine derivatives such as picoline, N-methylpyrrolidone, etc. Pyridine, N-methylpyrrolidone, etc. are used particularly preferably. The amount of the solvent used can be  
10 suitably determined depending on the start materials, the kind of base, reaction conditions, etc. Although the reaction temperature is not particularly limited in the method of the present invention, it is usually a temperature in the range of -20°C to the boiling  
15 point of the solvent. However, it is preferable to conduct reaction at the optimal temperature for the condensing agent to be used.

[0074]

In the method of the present invention, the  
20 range of reaction time is usually 1 to 48 hours. Particularly, 1 to 10 hours is preferable.

[0075]

In the present invention, collection and purification of the target polyhydroxyalkanoate from  
25 a reaction liquid containing the thus generated polyhydroxyalkanoate having a unit represented by the chemical formula (1) can be carried out by a normal

method such as distillation. Alternatively, the target polyhydroxyalkanoate represented by the chemical formula (1) can be precipitated by uniformly mixing a solvent such as water, alcohols such as 5 methanol and ethanol, ethers such as dimethyl ether, diethyl ether and tetrahydrofuran with the reaction liquid, and thereby collecting the same.

Polyhydroxyalkanoate having a unit represented by the chemical formula (1) obtained here can be isolated 10 and purified if required. As this isolating and purifying method, there is particularly no restriction and the method of re-precipitating using a solvent insoluble to polyhydroxyalkanoate having a unit represented by the chemical formula (1), method 15 by column chromatography, dialyzing method, etc. can be used.

[0076]

As another production method of the present invention, when R moiety in the chemical formula (1) 20 is  $-A_1-SO_3H$ , there is a method of performing methyl esterification to convert the R moiety in chemical formula (1) to  $-A_1-SO_3CH_3$  using a methyl esterification agent after condensation reaction with an amine. As a methyl esterification agent, those 25 used for methyl esterification of a fatty acid in gas chromatography analysis can be used. As a methyl esterification method, an acid catalyst method such

as hydrochloric acid-methanol method, boron trifluoride-methanol method and sulfuric acid-methanol method, a base catalyst method such as sodium methoxide method, tetramethylguanidine method and trimethylsilyldiazomethane method, etc., can be mentioned. Particularly, trimethylsilyldiazomethane method is preferable since methylation is possible under mild conditions.

[0077]

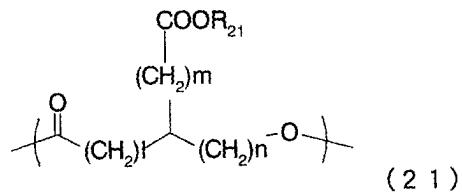
As for the solvent used in the reaction of the present invention, hydrocarbons such as hexane, cyclohexane and heptane, alcohols such as methanol and ethanol, halogenated hydrocarbons such as dichloromethane, chloroform, carbon tetrachloride, dichloroethane, and trichloroethane, aromatic hydrocarbons such as benzene and toluene, etc. can be mentioned. Halogenated hydrocarbons are used particularly preferably. The amount of the solvent used can be suitably determined depending on the starting materials, reaction conditions, etc. Although the reaction temperature is not particularly limited in the method of the present invention, it is usually a temperature in the range of -20°C to 30°C. However, it is preferable to conduct reaction at the optimal temperature for the condensing agent and reagent to be used.

[0078]

In the meantime, among the polyhydroxyalkanoate having a unit represented by the chemical formula (5) of the present invention, a polyhydroxyalkanoate having a unit represented by the chemical formula 5 (21) can be prepared by using a polyhydroxyalkanoate having a unit represented by the chemical formula (22) as a starting material and oxidizing a double bond moiety in the side chain of the polyhydroxyalkanoate.

10 [0079]

[chemical formula 28]

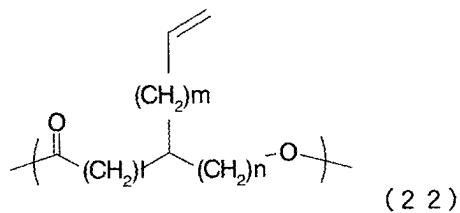


[0080]

wherein  $R_{21}$  is hydrogen or a salt forming group;  $l$  is 15 an integer selected from 1 to 4,  $n$  is an integer selected from 1 to 4,  $m$  is an integer selected from 0 to 8, when  $l$  is 1, 3, and 4,  $n$  is an integer selected from 1 to 4, and  $m$  is an integer selected from 0 to 8; and when  $l$  is 2 and  $n$  is 1, 3, and 4,  $m$  is an 20 integer selected from 0 to 8; and when  $l$  is 2 and  $n$  is 2,  $m$  is an integer selected from 1 to 8; and when two or more units are present,  $R_{21}$ ,  $l$ ,  $m$ , and  $n$  mean as above independently for every unit.

[0081]

[chemical formula 29]



[0082]

5 wherein l is an integer selected from 1 to 4, n is an integer selected from 1 to 4, m is an integer selected from 0 to 8, when l is 1, 3, and 4, n is an integer selected from 1 to 4, and m is an integer selected from 0 to 8; and when l is 2 and n is 1, 3,  
 10 and 4, m is an integer selected from 0 to 8; and when l is 2 and n is 2, m is an integer selected from 1 to 8; and when two or more units are present, l, m and n mean as above independently for every unit.

As a method of carrying out oxidative cleavage  
 15 of a carbon-carbon double bond by an oxidizing agent as above to obtain a carboxylic acid, for example, a method using a permanganic acid salt (J. Chem. Soc., Perkin. Trans. 1, 806 (1973)), a method using a dichromate (Org. Synth., 4, 698 (1963)), a method  
 20 using a periodic acid salt (J. Org. Chem., 46, 19 (1981)), a method using nitric acid (Japanese Patent Application Laid-Open No. S59-190945), a method using

ozone (J. Am. Chem. Soc., 81, 4273 (1959)) etc. are known. Macromolecular chemistry, 4,289-293 (2001) also reports a method of obtaining a carboxylic acid by reacting a carbon-carbon double bond at the end of 5 the side chain of polyhydroxyalkanoate produced by microorganisms using potassium permanganate as an oxidizing agent under acidic conditions. The same method can be used also in the present invention.

[0083]

10 As a permanganic acid salt used as an oxidizing agent, potassium permanganate is commonly used. The amount of a permanganic acid salt used may be usually 1 mol equivalent or more and preferably 2 to 10 mol equivalents per one mol of the unit represented by 15 the chemical formula (22), since the oxidative cleavage reaction is a stoichiometric reaction. In order to adjust the reaction system under acidic conditions, various kinds of inorganic acids and organic acids such as sulfuric acid, hydrochloric acid, acetic acid and nitric acid are usually used. 20 However, when acids such as sulfuric acid, nitric acid, hydrochloric acid and the like are used, ester bond in the main chain may be cleaved, which may cause a decrease in the molecular weight. Therefore, 25 it is preferable to use acetic acid. The amount of acid used is usually 0.2 to 2000 mol equivalent and preferably 0.4 to 1000 mol equivalent per one mol of

the unit represented by the chemical formula (22). When it is not less than 0.2 mol equivalent, preferable yield will be resulted, and when it is not more than 2000 mol equivalent, by-product material by 5 decomposition by acid can be reduced, and therefore, it is preferable to adjust it within the limits as defined above. Moreover, crown-ethers can be used in order to promote the reaction. In this case, crown-ether and permanganic acid salt form a complex, and 10 result in an increased reaction activity. As a crown-ether, dibenzo-18-crown-6-ether, dicyclo-18-crown-6-ether and 18-crown-6-ether are generally used. It is usually preferable to use the crown-ether in an amount of usually 0.005 to 2.0 mol equivalent, and 15 preferably 0.01 to 1.5 mol equivalent per one mol of permanganic acid salt.

[0084]

The solvent used in the oxidation reaction of the present invention is not particularly limited, as 20 long as it is a solvent inactive in the reaction, and, for example, water, acetone; ethers such as tetrahydrofuran and dioxane; aromatic hydrocarbons such as benzene; aliphatic hydrocarbons such as hexane and heptane; halogenated hydrocarbons such as 25 methyl chloride, dichloromethane and chloroform can be used. Among these solvents, if the solubility of polyhydroxyalkanoate is taken into consideration,

halogenated hydrocarbons such as methyl chloride, dichloromethane and chloroform and acetone are preferable.

[0085]

5       The polyhydroxyalkanoate having a unit represented by the chemical formula (22), permanganic acid salt and acid may be placed as a whole together with a solvent from the beginning or each of them may be continuously or intermittently added to the system  
10      to proceed the reaction in oxidation reaction of the present invention. In addition, only permanganic acid salt may be previously dissolved or suspended in a solvent, and subsequently polyhydroxyalkanoate and acid may be added to the system continuously or  
15      intermittently to proceed the reaction, or only polyhydroxyalkanoate may be previously dissolved or suspended in a solvent, and subsequently permanganic acid salt and acid may be added to the system continuously or intermittently to proceed the  
20      reaction. Furthermore, polyhydroxyalkanoate and acid may be placed previously, and subsequently permanganic acid salt may be added to the system continuously or intermittently to proceed the reaction, or permanganic acid salt and acid are  
25      placed previously, and subsequently polyhydroxyalkanoate may be added to the system continuously or intermittently to proceed the

reaction, or polyhydroxyalkanoate and permanganic acid salt are placed previously, and subsequently acid may be added to the system continuously or intermittently to proceed the reaction.

5 [0086]

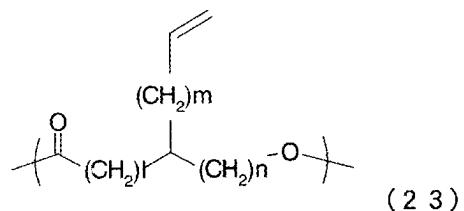
It is suitable to adjust the reaction temperature usually to -40 to 40°C, preferably -10 to 30°C. It is suitable to adjust the reaction time to usually 2 to 48 hours, although it is dependent on 10 the stoichiometric ratio of the unit represented by the chemical formula (22) and permanganic acid salt and the reaction temperature.

[0087]

In addition, polyhydroxyalkanoate containing a 15 unit represented by the chemical formula (24) can be prepared by oxidation reaction from polyhydroxyalkanoate containing a unit represented by the chemical formula (23) by the similar method as the above-described oxidation reaction. This 20 production method is a novel production method.

[0088]

[chemical formula 30]

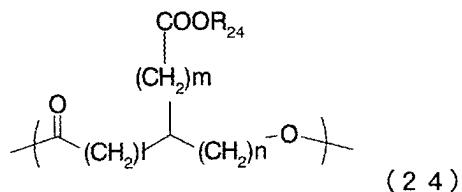


[0089]

wherein l is 2, n is 2, and m is 0.

[0090]

5 [chemical formula 31]



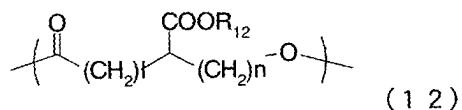
[0091]

wherein R<sub>24</sub> is hydrogen or a salt forming group; l is 2, n is 2, and m is 0.

10 Among the polyhydroxyalkanoates having a unit represented by the chemical formula (5), a polyhydroxyalkanoate having a unit represented by the chemical formula (12) can be also prepared by using polyhydroxyalkanoate having a unit represented by the 15 chemical formula (10) as a starting material by the method of hydrolyzing the side chain ester moiety in the presence of an acid or alkali, or by the method of hydrocracking including catalytic reduction.

[0092]

[chemical formula 32]

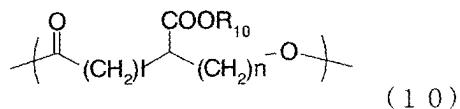


[0093]

5 wherein  $R_{12}$  is hydrogen or a salt forming group;  $l$  is  
an integer selected from 1 to 4,  $n$  is an integer  
selected from 1 to 4, and when  $l$  is 1, 3, and 4,  $n$  is  
an integer selected from 1 to 4, and when  $l$  is 2,  $n$   
is 1, 3, and 4; and when two or more units are  
10 present,  $l$ ,  $n$  and  $R_{12}$  mean as above independently for  
every unit.

[ 0094 ]

[chemical formula 33]



15 [0095]

wherein R<sub>10</sub> is a substituent selected from a linear or branched alkyl group having 1 to 12 carbon atoms or an aralkyl group; l is an integer selected from 1 to 4, n is an integer selected from 1 to 4, and when l is 1, 3 or 4, n is an integer selected from 1 to 4, and when l is 2, n is 1, 3 or 4; and when two or more

units are present, l, n and R<sub>10</sub> mean as above independently for every unit.

When a method of hydrolyzing in the presence of an acid or alkali is used, the method can be

5 performed using a solution of an inorganic acid such as hydrochloric acid, sulfuric acid, nitric acid or phosphoric acid, or an organic acid such as trifluoroacetic acid, trichloroacetic acid, p-toluenesulfonic acid and methanesulfonic acid in

10 water or an organic solvent having affinity to water such as methanol, ethanol, tetrahydrofuran, dioxane, dimethylformamide and dimethylsulfoxide, or alternatively using an aqueous solution of an aqueous caustic alkali such as sodium hydroxide and

15 potassium hydroxide or an alkali carbonate such as sodium carbonate and potassium carbonate or an alcoholic solution of metal alkoxide such as sodium methoxide and sodium ethoxide. It is suitable to adjust the reaction temperature usually to 0 to 40°C

20 and preferable to 0 to 30°C. It is suitable to adjust the reaction time usually to 0.5 to 48 hours. However, when hydrolyzation is conducted with an acid or alkali, ester bond in the main chain may be cleaved in any case and may cause decrease in

25 molecular weight.

[0096]

When a method of obtaining a carboxylic acid

using a method of hydrocracking including catalytic reduction is used, the method can be performed as follows. That is, hydrogen is made to act in the presence of a reduction catalyst under normal or

5 increased pressure in a proper solvent at a temperature from -20°C to the boiling point of the solvent used, preferably 0 to 50°C, and catalytic reduction is performed. Examples of the solvent to be used include water, methanol, ethanol, propanol,

10 hexafluoroisopropanol, ethyl acetate, diethyl ether, tetrahydrofuran, dioxane, benzene, toluene, dimethylformamide, pyridine, N-methylpyrrolidone, etc.

A mixed solvent of these solvents can also be used.

As a reduction catalyst, catalysts such as palladium,

15 platinum, rhodium, etc. by itself or supported on a carrier, or Raney nickel, can be used. It is suitable to adjust the reaction time usually to 0.5 to 72 hours. The thus formed reaction liquid containing a polyhydroxyalkanoate having a unit

20 represented by the chemical formula (10) is collected as a crude polymer by filtering off the catalyst and removing the solvent by distillation etc. The polyhydroxyalkanoate having a unit represented by the chemical formula (10) obtained here can be isolated

25 and purified if required. The method of isolation and purification is not particularly limited and a method of precipitating the polyhydroxyalkanoate

having a unit represented by the chemical formula  
(10) using a solvent which does not dissolve the polyhydroxyalkanoate, a method using column chromatography, a dialyzing method, etc. can be used.

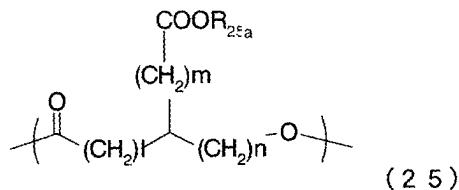
- 5 However, when catalytic reduction is used, ester bond  
in the main chain may be also cleaved and may cause a  
decrease in molecular weight.

[0097]

In addition, among the polyhydroxyalkanoates  
10 having a unit represented by the chemical formula (5),  
a polyhydroxyalkanoate having a unit represented by  
the chemical formula (25) can be prepared by  
esterifying a polyhydroxyalkanoate having a unit  
represented by the chemical formula (11) as a  
15 starting material using an esterification agent.

[0098]

[chemical formula 34]



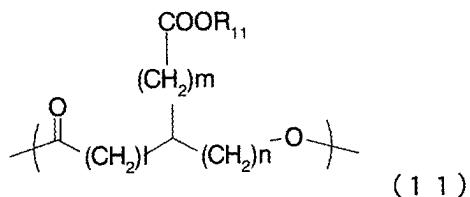
[0099]

- 20 wherein R<sub>25a</sub> is a linear or branched alkyl group having 1 to 12 carbon atoms or an aralkyl group or a substituent having a saccharide; l is an integer selected from 1 to 4, n is an integer selected from 1 to 4.

to 4, m is an integer selected from 0 to 8, and when l is 1, 3, and 4, n is an integer selected from 1 to 4, and m is an integer selected from 0 to 8; and when l is 2 and n is 1, 3, and 4, m is an integer selected  
 5 from 0 to 8; and when l is 2 and n is 2, m is an integer selected from 1 to 8; and when l is 2, n is 2 and m is 0, R<sub>25a</sub> is a substituent having a saccharide; and when two or more units are present, R<sub>25a</sub>, and l, m and n mean as above independently for every unit.

10 [0100]

[chemical formula 35]



[0101]

wherein R<sub>11</sub> is hydrogen or a salt forming group; l is  
 15 an integer selected from 1 to 4, n is an integer selected from 1 to 4, and m is an integer selected from 0 to 8; and when two or more units are present, l, m, n and R<sub>11</sub> mean as above independently for every unit.

20 As an esterification agent used, diazomethane and DMF dimethyl acetal can be used. For example, polyhydroxyalkanoate having a unit represented by the chemical formula (11) reacts easily with DMF dimethyl

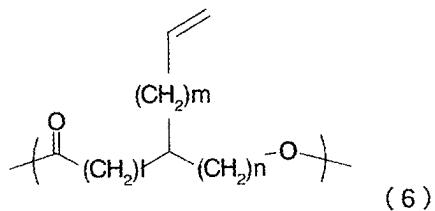
acetal, DMF diethyl acetal, DMF dipropyl acetal, DMF diisopropyl acetal, DMF-n-butyl acetal, DMF-tert-butyl acetal, or DMF dineopentyl acetal, and gives corresponding esters. In addition, an esterified polyhydroxyalkanoate can be obtained by performing a reaction with an alcohol, for example, methanol, ethanol, propanol, isopropyl alcohol, butyl alcohol, sec-butyl alcohol, tert-butyl alcohol, pentyl alcohol, neopentyl alcohol, hexyl alcohol, heptyl alcohol, octyl alcohol, nonyl alcohol, decyl alcohol and lauryl alcohol and saccharides for introducing a group having a saccharide structure, for example, D-glucose, D-fructose and other saccharides following a method using an acid catalyst or a condensing agent such as DCC.

[0102]

A polyhydroxyalkanoate represented by the chemical formula (6) of the present invention can be prepared by carrying out polymerization of an intramolecular closed ring compound of  $\omega$ -hydroxycarboxylic acid represented by the chemical formula (8) in the presence of a catalyst.

[0103]

[chemical formula 36]

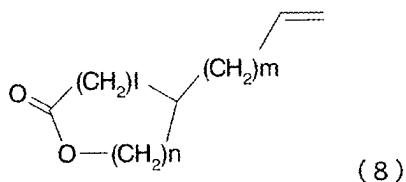


[0104]

wherein l is an integer selected from 1 to 4, n is an integer selected from 1 to 4, and m is an integer  
 5 selected from 0 to 8; and when two or more units are present, l, m and n mean as above independently for every unit.

[0105]

[chemical formula 37]



10

[0106]

wherein l is an integer selected from 1 to 4, n is an integer selected from 1 to 4, and m is an integer selected from 0 to 8.

15 In the production of a polyester containing a unit represented by the chemical formula (6) using an intramolecular closed ring compound of  $\omega$ -hydroxycarboxylic acid represented by the chemical formula (8) of the present invention, polymerization

method is not particularly limited and, for example, solution polymerization method, slurry polymerization method, mass polymerization method, etc. can be adopted. In addition, when a polymerization solvent is used, the solvent is not particularly limited and, for example, inert solvents such as aliphatic hydrocarbons and cyclic hydrocarbons having 5 to 18 carbon atoms, aromatic hydrocarbons having 6 to 20 carbon atoms, tetrahydrofuran, chloroform, o-dichlorobenzene, dioxane, etc. can be used.

Conventional ring-opening polymerization catalysts can be used as a catalyst used for this polymerization. Examples thereof include tin dichloride, tin tetrachloride, stannous fluoride, stannous acetate, stannous stearate, stannous octanoate, stannous oxide, stannic oxide, and other tin salts. In addition, triethoxyaluminum, tri-n-propoxyaluminum, tri-iso-propoxyaluminum, tri-n-butoxyaluminum, tri-iso-butoxyaluminum, aluminium chloride, di-iso-propyl zinc, dimethylzinc, diethylzinc, zinc chloride, tetra-n-propoxytitanium, tetra-n-butoxytitan, tetra-n-butoxytitan, tetra-t-butoxytitan, antimony trifluoride, lead oxide, lead stearate, titanium tetrachloride, boron trifluoride, boron trifluoride-ether complex, triethylamine, tributylamine, etc. can be mentioned.

The amount of these catalysts to be used is in the range of 0.0001 to 10% by weight, and preferably in the range of 0.001 to 5% by weight to the total amount of the monomer compound.

5 [0108]

In the present invention, conventional polymerization initiators can be used as a polymerization initiator on the occasion of ring-opening polymerization. Specifically, aliphatic alcohols may be any of mono-, di-, or polyhydric alcohols and may be saturated or unsaturated alcohols. Specifically, monoalcohols such as methanol, ethanol, propanol, butanol, pentanol, hexanol, heptanol, nonanol, decanol, lauryl alcohol, myristic alcohol, 15 cetyl alcohol, stearyl alcohol and p-tert-butylbenzyl alcohol, dialcohols such as ethylene glycol, butanediol, hexanediol, nonanediol and tetramethylene glycol, polyhydric alcohols such as glycerol, sorbitol, xylitol, ribitol and erythritol, and methyl lactate, ethyl lactate, etc. can be used. Although there are some differences according to the conditions depending on the alcohol used, these aliphatic alcohols can be usually used at a ratio of 0.01 to 10% by weight to the total amount of the 20 monomer. In the present invention, the temperature of ring-opening polymerization reaction is in the range of 25 to 200°C, preferably in the range of 50

to 200°C, more preferably in the range of 100 to 180°C.

[0109]

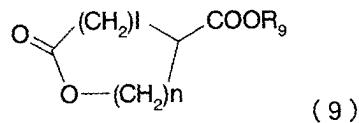
In the present invention, the ring-opening polymerization reaction may be performed under inert atmosphere such as nitrogen and argon, either reduced or increased pressure, and a catalyst and an alcohol may be added sequentially.

[0110]

In addition, the polyhydroxyalkanoate having a unit represented by the chemical formula (10) of the present invention can be prepared by carrying out polymerization of an intramolecular closed ring compound of  $\omega$ -hydroxycarboxylic acid represented by the chemical formula (9) in the presence of a catalyst.

[0111]

[chemical formula 38]



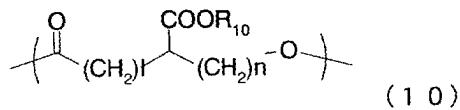
[0112]

wherein  $R_9$  is a substituent selected from a linear or branched alkyl group having 1 to 12 carbon atoms or an aralkyl group;  $l$  is an integer selected from 1 to 4,  $n$  is an integer selected from 1 to 4, and when  $l$

is 1, 3 or 4, n is an integer selected from 1 to 4,  
and when l is 2, n is 1, 3 or 4.

[0113]

[chemical formula 39]



5

[0114]

wherein  $\text{R}_{10}$  is a substituent selected from a linear  
or branched alkyl group having 1 to 12 carbon atoms  
or an aralkyl group; l is an integer selected from 1  
10 to 4, n is an integer selected from 1 to 4, and when  
l is 1, 3 or 4, n is an integer selected from 1 to 4,  
and when l is 2, n is 1, 3 or 4; and when two or more  
units are present, l and n mean as above  
independently for every unit.

15 In the production of a polyester containing a  
unit represented by the chemical formula (10) using  
an intramolecular closed ring compound of  $\omega$ -  
hydroxycarboxylic acid represented by the chemical  
formula (9) of the present invention, polymerization  
method is not particularly limited and, for example,  
20 solution polymerization method, slurry polymerization  
method, mass polymerization method, etc. can be  
adopted. In addition, when a polymerization solvent  
is used, the solvent is not particularly limited and,

for example, inert solvents such as aliphatic hydrocarbons and cyclic hydrocarbons having 5 to 18 carbon atoms, aromatic hydrocarbons having 6 to 20 carbon atoms, tetrahydrofuran, chloroform, o-dichlorobenzene, dioxane, etc. can be used.

[0115]

In the present invention, conventional ring-opening polymerization catalysts can be used as a catalyst for polymerization. Examples thereof include tin dichloride, tin tetrachloride, stannous fluoride, stannous acetate, stannous stearate, stannous octanoate, stannous oxide, stannic oxide, and other tin salts. In addition, triethoxyaluminum, tri-n-propoxy-aluminum, tri-iso-propoxyaluminum, tri-n-butoxyaluminum, tri-iso-butoxyaluminum, aluminium chloride, di-iso-propyl zinc, dimethylzinc, diethylzinc, zinc chloride, tetra-n-propoxytitanium, tetra-n-butoxytitan, tetra-n-butoxytitan, tetra-t-butoxytitan, antimony trifluoride, lead oxide, lead stearate, titanium tetrachloride, boron trifluoride, boron trifluoride-ether complex, triethylamine, tributylamine, etc. can be mentioned.

[0116]

The amount of these catalysts to be used is in the range of 0.0001 to 10% by weight, and preferably in the range of 0.001 to 5% by weight to the total amount of the monomer compound.

[0117]

In the present invention, conventional polymerization initiators can be used as a polymerization initiator on the occasion of ring-opening polymerization. Specifically, aliphatic alcohols may be any of mono-, di-, or polyhydric alcohols and may be saturated or unsaturated alcohols. Specifically, monoalcohols such as methanol, ethanol, propanol, butanol, pentanol, hexanol, heptanol, 10 nonanol, decanol, lauryl alcohol, myristic alcohol, cetyl alcohol, stearyl alcohol and p-tert-butylbenzyl alcohol, dialcohols such as ethylene glycol, butanediol, hexanediol, nonanediol and tetramethylene glycol, polyhydric alcohols such as glycerol, 15 sorbitol, xylitol, ribitol and erythritol, and methyl lactate, ethyl lactate, etc. can be used. Although there are some differences according to the conditions depending on the alcohol used, these aliphatic alcohols can be usually used at a ratio of 20 0.01 to 10% by weight to the total amount of the monomer. In the present invention, the temperature of ring-opening polymerization reaction is in the range of 25 to 200°C, preferably in the range of 50 to 200°C, more preferably in the range of 100 to 25 180°C.

[0118]

In the present invention, the ring-opening

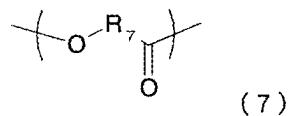
polymerization reaction may be performed under inert atmosphere such as nitrogen and argon, either reduced or increased pressure, and a catalyst and an alcohol may be added sequentially.

5 [0119]

Although the polyhydroxyalkanoate of the present invention is mainly composed of the unit represented by the chemical formula (1), (5) or (6) shown above, it may be also a copolymer to which a 10 second ingredient etc. is copolymerized in order to change various physical properties such as mechanical properties and decomposition characteristics. For example, a unit represented by the chemical formula (7) can be further contained in a molecule.

15 [0120]

[chemical formula 40]



[0121]

wherein R<sub>7</sub> is a linear or branched alkylene group 20 having 1 to 11 carbon atoms, an alkyleneoxyalkylene group, wherein each alkylene group is independently an alkylene group having 1 to 2 carbon atoms, respectively, or an alkylidene group having 1 to 5 carbon atoms which may be substituted with aryl; and

when two or more units are present, R<sub>7</sub> means as above independently for every unit.

As an example as the second ingredient, a cyclic diester of  $\alpha$ -hydroxycarboxylic acid or a lactone which is an intramolecular closed ring compound of  $\omega$ -hydroxycarboxylic acid can be copolymerized. Furthermore, specific examples of a cyclic diester of  $\alpha$ -hydroxycarboxylic acid include intermolecular cyclic diesters such as glycolide, lactide,  $\alpha$ -hydroxybutyric acid,  $\alpha$ -hydroxy-isobutyric acid,  $\alpha$ -hydroxyvaleric acid,  $\alpha$ -hydroxy-isovaleric acid,  $\alpha$ -hydroxy- $\alpha$ -methylbutyric acid,  $\alpha$ -hydroxycaproic acid,  $\alpha$ -hydroxy-isocaproic acid,  $\alpha$ -hydroxy- $\beta$ -methylvaleric acid,  $\alpha$ -hydroxyheptanoic acid, mandelic acid, and  $\beta$ -phenyllactic acid. As for the compounds having an asymmetric carbon, any of L-compound, D-compound, racemate and meso compound can be used. The cyclic diester may be also formed from different  $\alpha$ -oxy acid molecules. Specifically, a cyclic diester between glycolic acid and lactic acid, and 3-methyl-2,5-diketo-1,4-dioxane etc. can be mentioned. Non-limiting examples of a lactone which is an intramolecular closed ring compound of  $\omega$ -hydroxycarboxylic acid include  $\beta$ -propiolactone,  $\beta$ -butyrolactone,  $\beta$ -isovalerolactone,  $\beta$ -caprolactone,  $\beta$ -isocaprolactone,  $\beta$ -methyl- $\beta$ -valerolactone,  $\gamma$ -butyrolactone,  $\gamma$ -valerolactone,  $\delta$ -valerolactone,  $\delta$ -

caprolactone, 11-oxydecanoic acid lactone, p-dioxanone, 1,5-dioxepan-2-one.

[0122]

Although the number average molecular weight of  
5 polyhydroxyalkanoate obtained by polymerization may  
vary depending on the conditions such as a type and  
amount of polymerization catalyst, polymerization  
temperature and polymerization time, 1,000 to  
1,000,000 is preferable.

10 [0123]

The molecular weight of polyhydroxyalkanoate  
can be measured as a relative molecular weight as  
well as an absolute molecular weight. It can be  
simply measured by GPC (gel permeation  
15 chromatography), etc. As a specific measuring method  
by GPC, the above-mentioned polyhydroxyalkanoate is  
beforehand dissolved in a solvent which can dissolve  
the polyhydroxyalkanoate, and measurement is  
performed with a similar mobile phase. As a detector,  
20 a differential refraction detector (RI) and an  
ultraviolet detector (UV) can be used depending on  
the polyhydroxyalkanoate to be measured. The  
molecular weight can be determined as a relatively  
compared value with a standard sample (polystyrene,  
25 polymethyl methacrylate, etc.). As a solvent, any  
solvent which dissolves the polymer such as  
dimethylformamide (DMF), dimethylsulfoxide (DMSO),

chloroform, tetrahydrofuran (THF), toluene, and hexafluoroisopropanol (HFIP) may be selected. In the case of a polar solvent, measurement can be also performed while a salt is added.

5 [0124]

In the present invention, it is preferable to use a polyhydroxyalkanoate as mentioned above which has a ratio (Mw/Mn) of the weight average molecular weight (Mw) to the number average molecular weight (Mn) measured as mentioned above in the range of 1 to 10 10. 10.

It should be noted that the reaction solvent, reaction temperature, reaction time, purifying method, etc. in the chemical reaction of the present 15 invention are not limited to the above-mentioned method.

[Examples]

[0125]

Although the present invention is described in 20 more detail referring to Examples given below and, the method of the present invention is not limited only to these Examples.

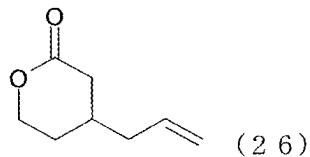
[0126]

(Example 1)

25 (Synthesis of polyester using tetrahydro-4-(2-propenyl)-2H-pyran-2-one represented by chemical formula (26))

[0127]

[chemical formula 41]



[0128]

5        1.40 g (0.01 mmol) of tetrahydro-4-(2-propenyl)-2H-pyran-2-one represented by the chemical formula (26), 4.0 ml of 0.01 M toluene solution of tin octylate (tin 2-ethylhexanoate), 4.0 ml of 0.01 M toluene solution of p-tert-butylbenzyl alcohol were  
10      placed in a polymerization ampoule and after performing drying under reduced pressure for 1 hour and nitrogen purge, it was heat-sealed under reduced pressure, and heated at 150°C to perform ring-opening polymerization. The reaction was ended after 12  
15      hours and the reaction product was cooled. The obtained polymer was dissolved in chloroform and reprecipitated in methanol in an amount of 10 times of the chloroform required for dissolving the polymer. The precipitation was collected and 0.53 g of polymer  
20      was obtained by carrying out drying under reduced pressure. In order to identify the structure of the obtained polymer, NMR analysis was performed on the following conditions.

<Measurement Apparatus> FT-NMR: Bruker DPX400

Resonant Frequency:  $^1\text{H}$  = 400 MHz

<Measurement Conditions> Nuclide Measured:  $^1\text{H}$

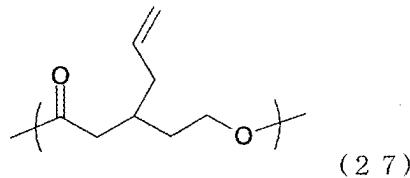
Solvent Used: TMS/CDCl<sub>3</sub>

Measurement Temperature: room temperature

5       Consequently, it was confirmed that the obtained compound was a polyhydroxyalkanoate which consists of a unit represented by the following chemical formula (27).

[0129]

10 [chemical formula 42]



[0130]

The average molecular weight of the obtained polyhydroxyalkanoate was estimated by gel permeation chromatography (GPC; TOSOH HLC-8220, column; TOSOH TSK-GEL Super HM-H, solvent; chloroform, polystyrene conversion). Consequently, the number average molecular weight, Mn was 6,200, and weight average molecular weight, Mw was 8,100.

20 [0131]

(Example 2)

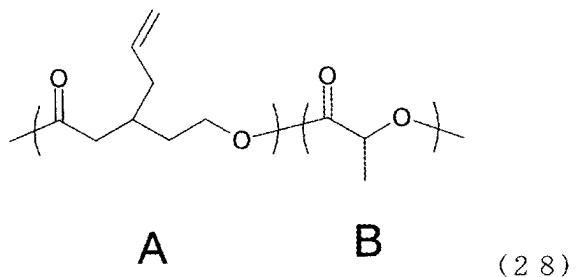
(Synthesis of polyester using tetrahydro-4-(2-propenyl)-2H-pyran-2-one and L-lactide)

0.28g (2.0 mmol) of tetrahydro-4-(2-propenyl)-

2H-pyran-2-one represented by the chemical formula (26), 1.44 g (10.0 mmol) of L-lactide, 4.8 ml of 0.01 M toluene solution of tin octylate (tin 2-ethylhexanoate), 4.8 ml of 0.01 M toluene solution of 5 p-tert-butylbenzyl alcohol were placed in a polymerization ampoule and after performing drying under reduced pressure for 1 hour and nitrogen purge, it was heat-sealed under reduced pressure, and heated at 150°C to perform ring-opening polymerization. The 10 reaction was ended after 12 hours and the reaction product was cooled. The obtained polymer was dissolved in chloroform and re-precipitated in methanol in an amount of 10 times of the chloroform required for dissolving the polymer. The 15 precipitation was collected and 1.19 g of polymer was obtained by carrying out drying under reduced pressure. In order to identify the structure of the obtained polymer, NMR analysis was performed on the same conditions as in Example 1 and consequently it 20 was confirmed that the obtained compound was a polyhydroxyalkanoate copolymer which contains a unit represented by the following chemical formula (28) as a monomer unit. It was also confirmed that the ratios of monomer units were 7 mol% for A unit and 93 25 mol% for B unit.

[0132]

[chemical formula 43]



[0133]

The average molecular weight of the obtained polyhydroxyalkanoate was estimated by gel permeation chromatography (GPC; TOSOH HLC-8220, column; TOSOH TSK-GEL Super HM-H, solvent; chloroform, polystyrene conversion). Consequently, the number average molecular weight, Mn was 21,500, and weight average molecular weight, Mw was 29,900.

10 [0134]

(Example 3)

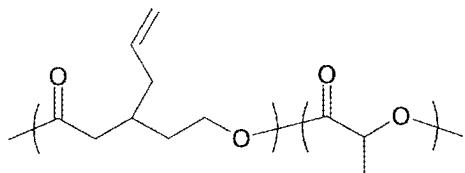
(Synthesis of polyester using tetrahydro-4-(2-propenyl)-2H-pyran-2-one and L-lactide)

14.0 g (10.0 mmol) of tetrahydro-4-(2-propenyl)-2H-pyran-2-one represented by the chemical formula (26), 7.21 g (50.0 mmol) of L-lactide, 2.4 ml of 0.1 M toluene solution of tin octylate (tin 2-ethylhexanoate), 2.4 ml of 0.1 M toluene solution of p-tert-butylbenzyl alcohol were placed in a polymerization ampoule and after performing drying under reduced pressure for 1 hour and nitrogen purge, it was heat-sealed under reduced pressure, and heated

at 150°C to perform ring-opening polymerization. The reaction was ended after 12 hours and the reaction product was cooled. The obtained polymer was dissolved in chloroform and re-precipitated in 5 methanol in an amount of 10 times of the chloroform required for dissolving the polymer. The precipitation was collected and 6.21 g of polymer was obtained by carrying out drying under reduced pressure. In order to identify the structure of the 10 obtained polymer, NMR analysis was performed on the same conditions as in Example 1 and consequently it was confirmed that the obtained compound was a polyhydroxyalkanoate copolymer which contains a unit represented by the following chemical formula (29) as 15 a monomer unit. It was also confirmed that the ratios of monomer units were 8 mol% for A unit and 92 mol% for B unit.

[0135]

[chemical formula 44]



A

B

(29)

20

[0136]

The average molecular weight of the obtained

polyhydroxyalkanoate was estimated by gel permeation chromatography (GPC; TOSOH HLC-8220, column; TOSOH TSK-GEL Super HM-H, solvent; chloroform, polystyrene conversion). Consequently, the number average

5 molecular weight, Mn was 23,200, and weight average molecular weight, Mw was 32,200.

[0137]

(Example 4)

(Synthesis of polyester using tetrahydro-4-(2-propenyl)-2H-pyran-2-one and mandelide (3,6-diphenyl-1,4-dioxane-2,5-dione))

0.28 g (2.0 mmol) of tetrahydro-4-(2-propenyl)-2H-pyran-2-one represented by the chemical formula (26), 2.68 g (10.0 mmol) of mandelide, 4.8 ml of 0.01 M toluene solution of tin octylate (tin 2-ethylhexanoate), 4.8 ml of 0.01 M toluene solution of p-tert-butylbenzyl alcohol were placed in a polymerization ampoule and after performing drying under reduced pressure for 1 hour and nitrogen purge, it was heat-sealed under reduced pressure, and heated at 150°C to perform ring-opening polymerization. The reaction was ended after 12 hours and the reaction product was cooled. The obtained polymer was dissolved in chloroform and re-precipitated in methanol in an amount of 10 times of the chloroform required for dissolving the polymer. The precipitation was collected and 1.79 g of polymer was

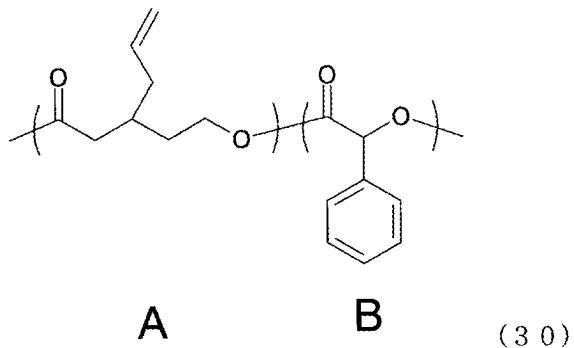
obtained by carrying out drying under reduced pressure.

[0138]

In order to identify the structure of the obtained polymer, NMR analysis was performed on the same conditions as in Example 1 and consequently it was confirmed that the obtained compound was a polyhydroxyalkanoate copolymer which contains a unit represented by the following chemical formula (30) as a monomer unit. It was also confirmed that the ratios of monomer units were 10 mol% for A unit and 90 mol% for B unit.

[0139]

[chemical formula 45]



15

[0140]

The average molecular weight of the obtained polyhydroxyalkanoate was estimated by gel permeation chromatography (GPC; TOSOH HLC-8220, column; TOSOH 20 TSK-GEL Super HM-H, solvent; chloroform, polystyrene

conversion). Consequently, the number average molecular weight, Mn was 18,700, and weight average molecular weight, Mw was 28,800.

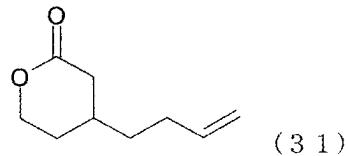
[0141]

5 (Example 5)

(Synthesis of polyester using tetrahydro-4-(2-butenyl)-2H-pyran-2-one represented by chemical formula (31) and  $\delta$ -valerolactone)

[0142]

10 [chemical formula 46]



[0143]

0.28 g (2.0 mmol) of tetrahydro-4-(3-butenyl)-2H-pyran-2-one represented by the chemical formula 15 (31), 1.00 g (10.0 mmol) of  $\delta$ -valerolactone, 4.8 ml of 0.01 M toluene solution of tin octylate (tin 2-ethylhexanoate), 4.8 ml of 0.01 M toluene solution of p-tert-butylbenzyl alcohol were placed in a polymerization ampoule and after performing drying 20 under reduced pressure for 1 hour and nitrogen purge, it was heat-sealed under reduced pressure, and heated at 150°C to perform ring-opening polymerization. The reaction was ended after 12 hours and the reaction product was cooled. The obtained polymer was

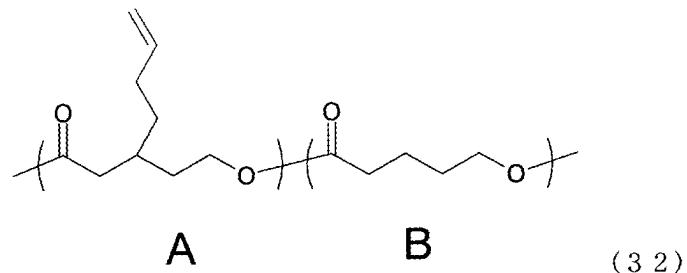
dissolved in chloroform and re-precipitated in methanol in an amount of 10 times of the chloroform required for dissolving the polymer. The precipitation was collected and 0.89 g of polymer was 5 obtained by carrying out drying under reduced pressure.

[0144]

In order to identify the structure of the obtained polymer, NMR analysis was performed on the 10 same conditions as in Example 1 and consequently it was confirmed that the obtained compound was a polyhydroxyalkanoate copolymer which contains a unit represented by the following chemical formula (32) as a monomer unit. It was also confirmed that the 15 ratios of monomer units were 14 mol% for A unit and 86 mol% for B unit.

[0145]

[chemical formula 47]



20 [0146]

The average molecular weight of the obtained

polyhydroxyalkanoate was estimated by gel permeation chromatography (GPC; TOSOH HLC-8220, column; TOSOH TSK-GEL Super HM-H, solvent; chloroform, polystyrene conversion). Consequently, the number average 5 molecular weight, Mn was 21,000, and weight average molecular weight, Mw was 29,000.

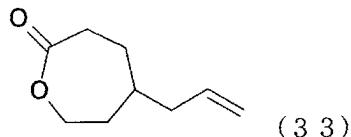
[0147]

(Example 6)

(Synthesis of polyester using 5-(2-propenyl)-2-oxepanone represented by chemical formula (33) and  $\epsilon$ -caprolactone)

[0148]

[chemical formula 48]



15 [0149]

0.34 g (2.0 mmol) of 5-(2-propenyl)-2-oxepanone represented by the chemical formula (33), 1.14 g (10.0 mmol) of  $\epsilon$ -caprolactone, 4.8 ml of 0.01 M toluene solution of tin octylate (tin 2-ethylhexanoate), 4.8 ml of 0.01 M toluene solution of p-tert-butylbenzyl alcohol were placed in a polymerization ampoule and after performing drying under reduced pressure for 1 hour and nitrogen purge, it was heat-sealed under reduced pressure, and heated

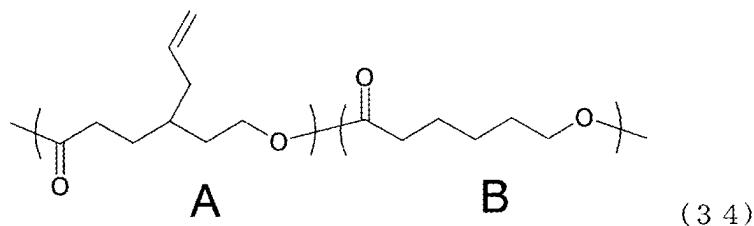
at 150°C to perform ring-opening polymerization. The reaction was ended after 12 hours and the reaction product was cooled. The obtained polymer was dissolved in chloroform and re-precipitated in 5 methanol in an amount of 10 times of the chloroform required for dissolving the polymer. The precipitation was collected and 0.96 g of polymer was obtained by carrying out drying under reduced pressure.

10 [0150]

In order to identify the structure of the obtained polymer, NMR analysis was performed on the same conditions as in Example 1 and consequently it was confirmed that the obtained compound was a 15 polyhydroxyalkanoate copolymer which contains a unit represented by the following chemical formula (34) as a monomer unit. It was also confirmed that the ratios of monomer units were 13 mol% for A unit and 87 mol% for B unit.

20 [0151]

[chemical formula 49]



[0152]

The average molecular weight of the obtained polyhydroxyalkanoate was estimated by gel permeation chromatography (GPC; TOSOH HLC-8220, column; TOSOH 5 TSK-GEL Super HM-H, solvent; chloroform, polystyrene conversion). Consequently, the number average molecular weight, Mn was 22,500, and weight average molecular weight, Mw was 32,000.

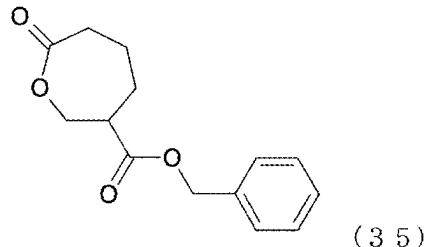
[0153]

10 (Example 7)

(Synthesis of polyester using 7-oxo-3-oxepane carboxylic acid phenylmethyl ester represented by chemical formula (35) and  $\epsilon$ -caprolactone)

[0154]

15 [chemical formula 50]



[0155]

0.50 g (2.0 mmol) of 7-oxo-3-oxepane carboxylic acid phenylmethyl ester represented by the chemical formula (35), 1.14 g (10.0 mmol) of  $\epsilon$ -caprolactone, 20 4.8 ml of 0.01 M toluene solution of tin octylate (tin 2-ethylhexanoate), 4.8 ml of 0.01 M toluene

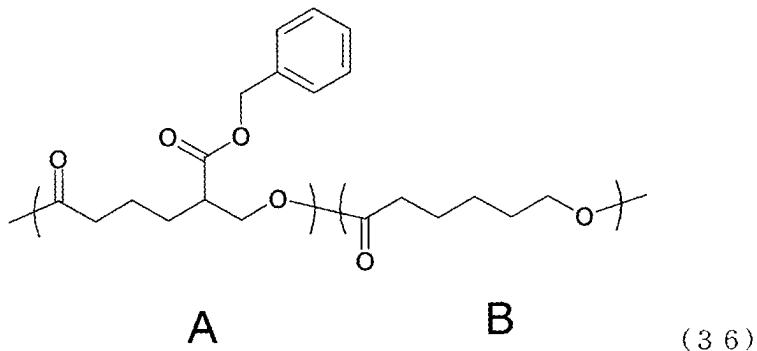
solution of p-tert-butylbenzyl alcohol were placed in a polymerization ampoule and after performing drying under reduced pressure for 1 hour and nitrogen purge, it was heat-sealed under reduced pressure, and heated  
5 at 150°C to perform ring-opening polymerization. The reaction was ended after 12 hours and the reaction product was cooled. The obtained polymer was dissolved in chloroform and re-precipitated in methanol in an amount of 10 times of the chloroform  
10 required for dissolving the polymer. The precipitation was collected and 1.23 g of polymer was obtained by carrying out drying under reduced pressure.

[0156]

15 In order to identify the structure of the obtained polymer, NMR analysis was performed on the same conditions as in Example 1 and consequently it was confirmed that the obtained compound was a polyhydroxyalkanoate copolymer which contains a unit represented by the following chemical formula (36) as  
20 a monomer unit. It was also confirmed that the ratios of monomer units were 14 mol% for A unit and 86 mol% for B unit.

[0157]

25 [chemical formula 51]



[0158]

The average molecular weight of the obtained polyhydroxyalkanoate was estimated by gel permeation chromatography (GPC; TOSOH HLC-8220, column; TOSOH TSK-GEL Super HM-H, solvent; chloroform, polystyrene conversion). Consequently, the number average molecular weight, Mn was 12,000, and weight average molecular weight, Mw was 16,000.

10 [0159]

1.00 g of the polyhydroxyalkanoate copolymer represented by the chemical formula (36) obtained here was dissolved in 100 ml of a mixed solvent of dioxane-ethanol (75:25), and 0.22 g of 5% palladium/carbon catalyst was added to this, the inside of the reaction system was filled with hydrogen, and the reaction mixture was agitated at room temperature for one day. After the reaction ended, the reaction mixture was filtered with a 0.25  $\mu\text{m}$  membrane filter in order to remove the catalyst,

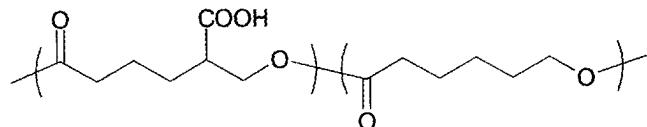
and the reaction solution was collected. After the solution was condensed, it was dissolved in chloroform, re-precipitation was performed using methanol in an amount of 10 times thereof. The 5 obtained polymer was collected and 0.75 g of polymer was obtained by carrying out drying under reduced pressure.

[0160]

In order to identify the structure of the 10 obtained polymer, NMR analysis was performed on the same conditions as in Example 1 and consequently it was confirmed that the obtained compound was a polyhydroxyalkanoate copolymer which contains a unit represented by the following chemical formula (37) as 15 a monomer unit. It was also confirmed that the ratios of monomer units were 14 mol% for C unit and 86 mol% for D unit.

[0161]

[chemical formula 52]



C

D

(37)

20

[0162]

The average molecular weight of the obtained

polyhydroxyalkanoate was estimated by gel permeation chromatography (GPC; TOSOH HLC-8220, column; TOSOH TSK-GEL Super HM-H, solvent; chloroform, polystyrene conversion). Consequently, the number average

5 molecular weight, Mn was 10,600, and weight average molecular weight, Mw was 14,700.

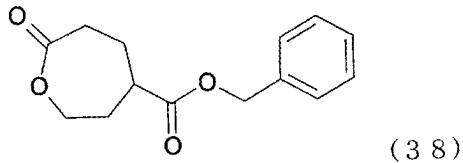
[0163]

(Example 8)

10 (Synthesis of polyester using 7-oxo-4-oxepane carboxylic acid phenylmethyl ester represented by chemical formula (38) and  $\epsilon$ -caprolactone)

[0164]

[chemical formula 53]



15 [0165]

2.48 g (10.0 mmol) of 7-oxo-4-oxepane carboxylic acid phenylmethyl ester represented by the chemical formula (38), 7.21 g (50.0 mmol) of L-lactide, 2.4 ml of 0.1 M toluene solution of tin octylate (tin 2-ethylhexanoate), 2.4 ml of 0.1 M toluene solution of p-tert-butylbenzyl alcohol were placed in a polymerization ampoule and after performing drying under reduced pressure for 1 hour and nitrogen purge, it was heat-sealed under reduced

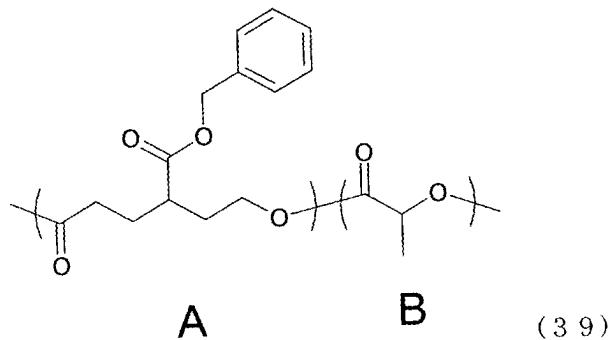
pressure, and heated at 150°C to perform ring-opening polymerization. The reaction was ended after 12 hours and the reaction product was cooled. The obtained polymer was dissolved in chloroform and re-  
5 precipitated in methanol in an amount of 10 times of the chloroform required for dissolving the polymer. The precipitation was collected and 7.08 g of polymer was obtained by carrying out drying under reduced pressure.

10 [0166]

In order to identify the structure of the obtained polymer, NMR analysis was performed on the same conditions as in Example 1 and consequently it was confirmed that the obtained compound was a  
15 polyhydroxyalkanoate copolymer which contains a unit represented by the following chemical formula (39) as a monomer unit. It was also confirmed that the ratios of monomer units were 8 mol% for A unit and 92 mol% for B unit.

20 [0167]

[chemical formula 54]



[0168]

The average molecular weight of the obtained polyhydroxyalkanoate was estimated by gel permeation chromatography (GPC; TOSOH HLC-8220, column; TOSOH TSK-GEL Super HM-H, solvent; chloroform, polystyrene conversion). Consequently, the number average molecular weight, Mn was 10,300, and weight average molecular weight, Mw was 14,800.

10 [0169]

5.00 g of the polyhydroxyalkanoate copolymer represented by the chemical formula (39) obtained here was dissolved in 500 ml of a mixed solvent of dioxane-ethanol (75:25), and 1.10 g of 5% palladium/carbon catalyst was added to this, the inside of the reaction system was filled with hydrogen, and the reaction mixture was agitated at room temperature for one day. After the reaction ended, the reaction mixture was filtered with a 0.25  $\mu\text{m}$  membrane filter in order to remove the catalyst, and the reaction solution was collected. After the

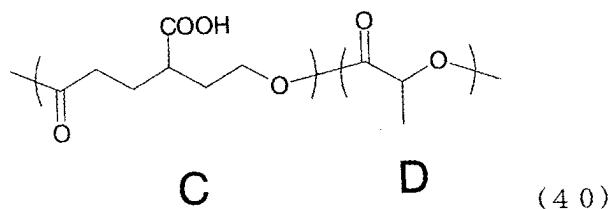
solution was condensed, it was dissolved in chloroform, re-precipitation was performed using methanol in an amount of 10 times thereof. The obtained polymer was collected and 3.70 g of polymer  
 5 was obtained by carrying out drying under reduced pressure.

[0170]

In order to identify the structure of the obtained polymer, NMR analysis was performed on the  
 10 same conditions as in Example 1 and consequently it was confirmed that the obtained compound was a polyhydroxyalkanoate copolymer which contains a unit represented by the following chemical formula (40) as a monomer unit. It was also confirmed that the  
 15 ratios of monomer units were 8 mol% for C unit and 92 mol% for D unit.

[0171]

[chemical formula 55]



20 [0172]

The average molecular weight of the obtained polyhydroxyalkanoate was estimated by gel permeation

chromatography (GPC; TOSOH HLC-8220, column; TOSOH TSK-GEL Super HM-H, solvent; chloroform, polystyrene conversion). Consequently, the number average molecular weight, Mn was 9,500, and weight average 5 molecular weight, Mw was 12,900.

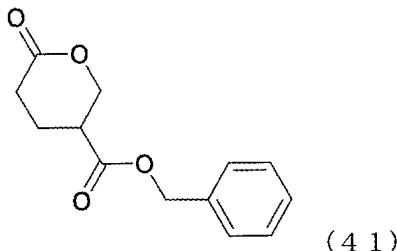
[0173]

(Example 9)

(Synthesis of polyester using tetrahydro-6-oxo-2H-pyran-3-carboxylic acid phenylmethyl ester 10 represented by chemical formula (41) and mandelide)

[0174]

[chemical formula 56]



[0175]

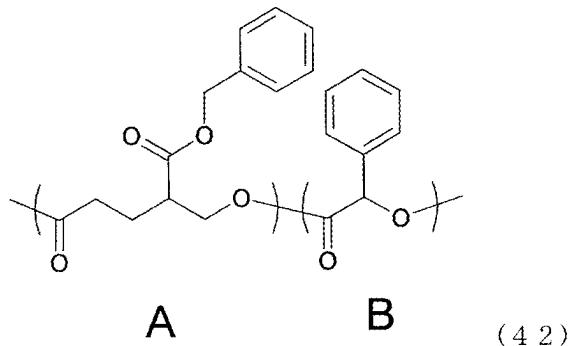
15        0.47g (2.0 mmol) of tetrahydro-6-oxo-2H-pyran-3-carboxylic acid phenylmethyl ester represented by the chemical formula (41), 2.68 g (10.0 mmol) of mandelide, 4.8 ml of 0.01 M toluene solution of tin octylate (tin 2-ethylhexanoate), 4.8 ml of 0.01 M toluene solution of p-tert-butylbenzyl alcohol were placed in a polymerization ampoule and after performing drying under reduced pressure for 1 hour

and nitrogen purge, it was heat-sealed under reduced pressure, and heated at 150°C to perform ring-opening polymerization. The reaction was ended after 12 hours and the reaction product was cooled. The 5 obtained polymer was dissolved in chloroform and re-precipitated in methanol in an amount of 10 times of the chloroform required for dissolving the polymer. The precipitation was collected and 2.06 g of polymer was obtained by carrying out drying under reduced 10 pressure.

In order to identify the structure of the obtained polymer, NMR analysis was performed on the same conditions as in Example 1 and consequently it was confirmed that the obtained compound was a 15 polyhydroxyalkanoate copolymer which contains a unit represented by the following chemical formula (42) as a monomer unit. It was also confirmed that the ratios of monomer units were 7 mol% for A unit and 93 mol% for B unit.

20 [0176]

[chemical formula 57]



[0177]

The average molecular weight of the obtained polyhydroxyalkanoate was estimated by gel permeation chromatography (GPC; TOSOH HLC-8220, column; TOSOH TSK-GEL Super HM-H, solvent; chloroform, polystyrene conversion). Consequently, the number average molecular weight, Mn was 12,000, and weight average molecular weight, Mw was 16,000.

10 [0178]

1.00 g of the polyhydroxyalkanoate copolymer represented by the chemical formula (42) obtained here was dissolved in 100 ml of a mixed solvent of dioxane-ethanol (75:25), and 0.22 g of 5% palladium/carbon catalyst was added to this, the inside of the reaction system was filled with hydrogen, and the reaction mixture was agitated at room temperature for one day. After the reaction ended, the reaction mixture was filtered with a 0.25  $\mu\text{m}$  membrane filter in order to remove the catalyst,

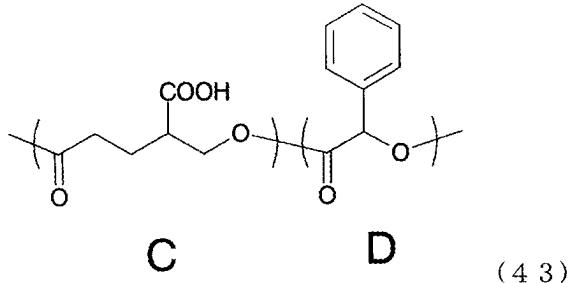
and the reaction solution was collected. After the solution was condensed, it was dissolved in chloroform, re-precipitation was performed using methanol in an amount of 10 times thereof. The obtained polymer was collected and 0.73 g of polymer was obtained by carrying out drying under reduced pressure.

[0179]

In order to identify the structure of the obtained polymer, NMR analysis was performed on the same conditions as in Example 1 and consequently it was confirmed that the obtained compound was a polyhydroxyalkanoate copolymer which contains a unit represented by the following chemical formula (43) as a monomer unit. It was also confirmed that the ratios of monomer units were 7 mol% for C unit and 93 mol% for D unit.

[0180]

[chemical formula 58]



20

[0181]

The average molecular weight of the obtained

polyhydroxyalkanoate was estimated by gel permeation chromatography (GPC; TOSOH HLC-8220, column; TOSOH TSK-GEL Super HM-H, solvent; chloroform, polystyrene conversion). Consequently, the number average 5 molecular weight, Mn was 8,700, and weight average molecular weight, Mw was 12,900.

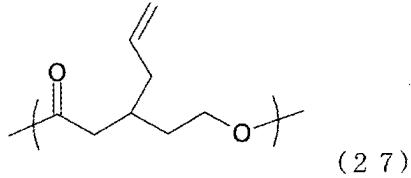
[0182]

(Example 10)

Oxidation reaction of polyhydroxyalkanoate 10 which consists of a unit represented by chemical formula (27) synthesized in Example 1

[0183]

[chemical formula 59]



15 [0184]

0.50 g of polyhydroxyalkanoate which consists of a unit represented by the chemical formula (27) obtained in Example 1 was added to an eggplant flask and dissolved with 30 ml of acetone added. This was 20 placed in an ice bath, and 5 ml of acetic acid and 2.83 g of 18-crown-6-ether were added and the mixture was agitated. Next, 2.25 g of potassium permanganate was slowly added on the ice bath, and agitated in an

ice bath for 2 hours, and agitated at room temperature for further 18 hours. 60 ml of ethyl acetate was added after the reaction ended, and 45 ml of water was further added. Next, sodium hydrogen sulfite was added until peracid was removed. Then, the pH of the liquid was adjusted to 1 with 1.0 N hydrochloric acid. The organic layer was extracted and washed 3 times with 1.0 N hydrochloric acid.

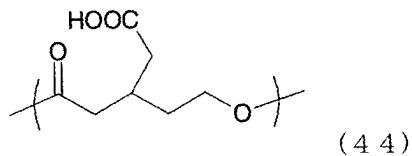
5 After the organic layer was collected, crude polymer was collected by evaporating the solvent. Next, 10 polymer was collected, after washed with 50 ml of water, 50 ml of methanol and further with 50 ml of water 3 times. Next, it was dissolved in 3 ml of THF, re-precipitation was performed using methanol in an 15 amount of 50 times of THF required for dissolving the polymer. The precipitation was collected and 0.42 g of polymer was obtained by carrying out drying under reduced pressure.

[0185]

20 In order to identify the structure of the obtained polymer, NMR analysis was performed on the same conditions as in Example 1 and consequently it was confirmed that the obtained compound was a polyhydroxyalkanoate which contains a unit 25 represented by the following chemical formula (44) as a monomer unit.

[0186]

[chemical formula 60]



[0187]

The average molecular weight of the obtained  
 5 polyhydroxyalkanoate was estimated by gel permeation chromatography (GPC; TOSOH HLC-8220, column; TOSOH TSK-GEL Super HM-H, solvent; chloroform, polystyrene conversion). Consequently, the number average  
 10 molecular weight, Mn was 4,700, and weight average  
 10 molecular weight, Mw was 6,200.

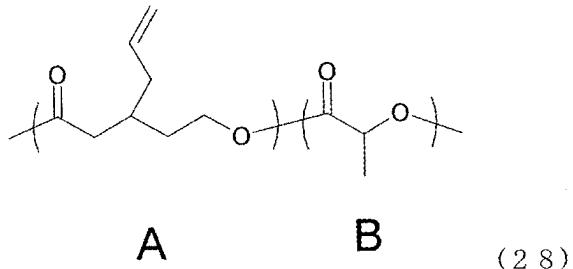
[0188]

(Example 11)

Oxidation reaction of polyhydroxyalkanoate  
 which consists of a unit represented by chemical  
 15 formula (28) synthesized in Example 2

[0189]

[chemical formula 61]



[0190]

0.50 g of a polyhydroxyalkanoate copolymer which consists of a unit represented by the chemical formula (28) (A: 7 mol%, B: 93 mol%) obtained in Example 2 was added to an eggplant flask and dissolved with 30 ml of acetone added. This was placed in an ice bath, and 5 ml of acetic acid and 0.36 g of 18-crown-6-ether were added and the mixture was agitated. Next, 0.28 g of potassium permanganate was slowly added on the ice bath, and agitated in an ice bath for 2 hours, and agitated at room temperature for further 18 hours. 60 ml of ethyl acetate was added after the reaction ended, and 45 ml of water was further added. Next, sodium hydrogen sulfite was added until peracid was removed. Then, the pH of the liquid was adjusted to 1 with 1.0 N hydrochloric acid. The organic layer was extracted and washed 3 times with 1.0 N hydrochloric acid. After the organic layer was collected, crude polymer was collected by evaporating the solvent. Next, polymer was collected, after washed with 50 ml of water, 50 ml of methanol and further with 50 ml of water 3 times. Next, it was dissolved in 3 ml of THF, re-precipitation was performed using methanol in an amount of 50 times of THF required for dissolving the polymer. The precipitation was collected and 0.43 g of polymer was obtained by carrying out drying under

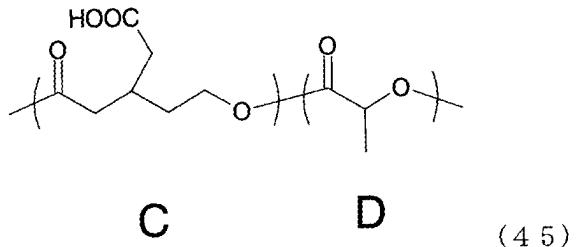
reduced pressure.

[0191]

In order to identify the structure of the obtained polymer, NMR analysis was performed on the 5 same conditions as in Example 1 and consequently it was confirmed that the obtained compound was a polyhydroxyalkanoate which contains a unit represented by the following chemical formula (45) as a monomer unit.

10 [0192]

[chemical formula 62]



[0193]

The average molecular weight of the obtained 15 polyhydroxyalkanoate was estimated by gel permeation chromatography (GPC; TOSOH HLC-8220, column; TOSOH TSK-GEL Super HM-H, solvent; chloroform, polystyrene conversion). Consequently, the number average molecular weight, Mn was 17,400, and weight average 20 molecular weight, Mw was 23,800.

[0194]

In order to calculate the unit of the obtained

polyhydroxyalkanoate furthermore, carboxyl groups at the end of the side chains of the polyhydroxyalkanoate were subjected to methyl esterification using trimethylsilyldiazomethane and 5 the calculation was performed.

[0195]

30 mg of the target polyhydroxyalkanoate was added to 100 ml-volume eggplant flask and dissolved with 2.1 ml of chloroform and 0.7 ml of methanol 10 added. 0.5 ml of 2 mol/L trimethylsilyldiazomethane-hexane solution was added to this, and agitated at room temperature for 1 hour. After the reaction ended, the solvent was removed and the polymer was collected. It was washed with 50 ml of methanol and 15 the polymer was collected after that. 30 mg of polyhydroxyalkanoate was obtained by carrying out drying under reduced pressure.

[0196]

In order to identify the structure of the 20 obtained polymer, NMR analysis was performed on the same conditions as in Example 1 and consequently it was confirmed that the obtained polyhydroxyalkanoate represented by the chemical formula (45) was a copolymer having a monomer ratio of 7 mol% for C unit 25 and 93 mol% for D unit.

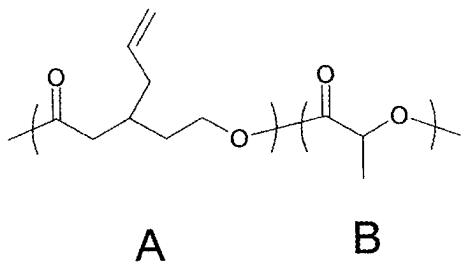
[0197]

(Example 12)

Oxidation reaction of polyhydroxyalkanoate  
which consists of a unit represented by chemical  
formula (29) synthesized in Example 3

[0198]

5 [chemical formula 63]



[0199]

5.00 g of a polyhydroxyalkanoate copolymer  
which consists of a unit represented by the chemical  
10 formula (29) (A: 8 mol%, B: 92 mol%) obtained in  
Example 3 was added to an eggplant flask and  
dissolved with 300 ml of acetone added. This was  
placed in an ice bath, and 50 ml of acetic acid and  
4.09 g of 18-crown-6-ether were added and the mixture  
15 was agitated. Next, 3.26 g of potassium permanganate  
was slowly added on the ice bath, and agitated in an  
ice bath for 2 hours, and agitated at room  
temperature for further 18 hours. 600 ml of ethyl  
acetate was added after the reaction ended, and 450  
20 ml of water was further added. Next, sodium hydrogen  
sulfite was added until peracid was removed. Then,  
the pH of the liquid was adjusted to 1 with 1.0 N

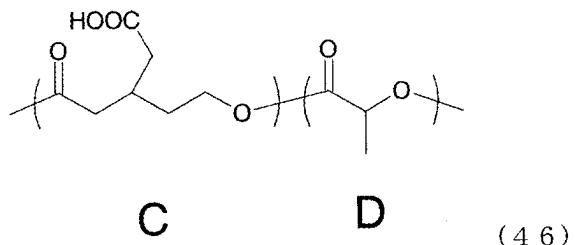
hydrochloric acid. The organic layer was extracted and washed 3 times with 1.0 N hydrochloric acid. After the organic layer was collected, crude polymer was collected by evaporating the solvent. Next, 5 polymer was collected, after washed with 500 ml of water, 500 ml of methanol and further with 500 ml of water 3 times. Next, it was dissolved in 30 ml of THF, re-precipitation was performed using methanol in an amount of 50 times of THF required for dissolving 10 the polymer. The precipitation was collected and 4.38 g of polymer was obtained by carrying out drying under reduced pressure.

[0200]

In order to identify the structure of the 15 obtained polymer, NMR analysis was performed on the same conditions as in Example 1 and consequently it was confirmed that the obtained compound was a polyhydroxyalkanoate which contains a unit represented by the following chemical formula (46) as 20 a monomer unit.

[0201]

[chemical formula 64]



[0202]

The average molecular weight of the obtained polyhydroxyalkanoate was estimated by gel permeation chromatography (GPC; TOSOH HLC-8220, column; TOSOH TSK-GEL Super HM-H, solvent; chloroform, polystyrene conversion). Consequently, the number average molecular weight, Mn was 19,800, and weight average molecular weight, Mw was 27,900.

10 [0203]

In order to calculate the unit of the obtained polyhydroxyalkanoate furthermore, carboxyl groups at the end of the side chains of the polyhydroxyalkanoate were subjected to methyl esterification using trimethylsilyldiazomethane and the calculation was performed.

[0204]

30 mg of the target polyhydroxyalkanoate was added to 100 ml-volume eggplant flask and dissolved with 2.1 ml of chloroform and 0.7 ml of methanol added. 0.5 ml of 2 mol/L trimethylsilyldiazomethane-hexane solution was added to this, and agitated at

room temperature for 1 hour. After the reaction ended, the solvent was removed and the polymer was collected. It was washed with 50 ml of methanol and the polymer was collected after that. 30 mg of 5 polyhydroxyalkanoate was obtained by carrying out drying under reduced pressure.

[0205]

In order to identify the structure of the obtained polymer, NMR analysis was performed on the 10 same conditions as in Example 1 and consequently it was confirmed that the obtained polyhydroxyalkanoate represented by the chemical formula (46) was a copolymer having a monomer ratio of 8 mol% for C unit and 92 mol% for D unit.

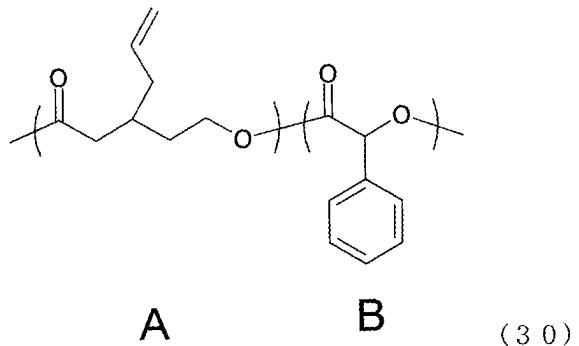
15 [0206]

(Example 13)

Oxidation reaction of polyhydroxyalkanoate which consists of a unit represented by chemical formula (30) synthesized in Example 4

20 [0207]

[chemical formula 65]



[0208]

0.50 g of a polyhydroxyalkanoate copolymer which consists of a unit represented by the chemical formula (30) (A: 10 mol%, B: 90 mol%) obtained in Example 4 was added to an eggplant flask and dissolved with 30 ml of acetone added. This was placed in an ice bath, and 5 ml of acetic acid and 0.29 g of 18-crown-6-ether were added and the mixture was agitated. Next, 0.23 g of potassium permanganate was slowly added on the ice bath, and agitated in an ice bath for 2 hours, and agitated at room temperature for further 18 hours. 60 ml of ethyl acetate was added after the reaction ended, and 45 ml of water was further added. Next, sodium hydrogen sulfite was added until peracid was removed. Then, the pH of the liquid was adjusted to 1 with 1.0 N hydrochloric acid. The organic layer was extracted and washed 3 times with 1.0 N hydrochloric acid.

After the organic layer was collected, crude polymer

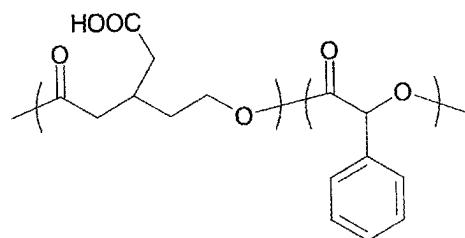
was collected by evaporating the solvent. Next, polymer was collected, after washed with 50 ml of water, 50 ml of methanol and further with 50 ml of water 3 times. Next, it was dissolved in 3 ml of THF, 5 re-precipitation was performed using methanol in an amount of 50 times of THF required for dissolving the polymer. The precipitation was collected and 0.41 g of polymer was obtained by carrying out drying under reduced pressure.

10 [0209]

In order to identify the structure of the obtained polymer, NMR analysis was performed on the same conditions as in Example 1 and consequently it was confirmed that the obtained compound was a 15 polyhydroxyalkanoate which contains a unit represented by the following chemical formula (47) as a monomer unit.

[0210]

[chemical formula 66]



C

D

(47)

[0211]

The average molecular weight of the obtained polyhydroxyalkanoate was estimated by gel permeation chromatography (GPC; TOSOH HLC-8220, column; TOSOH 5 TSK-GEL Super HM-H, solvent; chloroform, polystyrene conversion). Consequently, the number average molecular weight, Mn was 15,500, and weight average molecular weight, Mw was 20,300.

[0212]

10 In order to calculate the unit of the obtained polyhydroxyalkanoate furthermore, carboxyl groups at the end of the side chains of the polyhydroxyalkanoate were subjected to methyl esterification using trimethylsilyldiazomethane and 15 the calculation was performed.

[0213]

30 mg of the target polyhydroxyalkanoate was added to 100 ml-volume eggplant flask and dissolved with 2.1 ml of chloroform and 0.7 ml of methanol 20 added. 0.5 ml of 2 mol/L trimethylsilyldiazomethane-hexane solution was added to this, and agitated at room temperature for 1 hour. After the reaction ended, the solvent was removed and the polymer was collected. It was washed with 50 ml of methanol and 25 the polymer was collected after that. 28 mg of polyhydroxyalkanoate was obtained by carrying out drying under reduced pressure.

[0214]

NMR analysis was performed on the same conditions as in Example 1 and consequently it was confirmed that the obtained polyhydroxyalkanoate 5 represented by the chemical formula (47) was a copolymer having a monomer ratio of 10 mol% for C unit and 90 mol% for D unit.

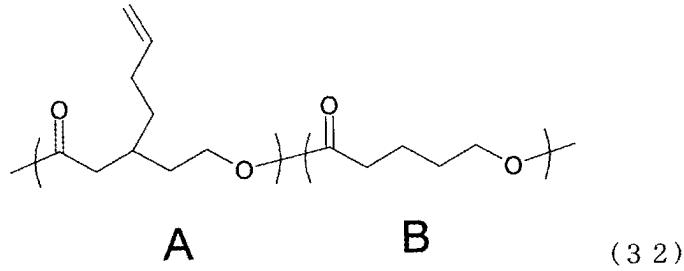
[0215]

(Example 14)

10 Oxidation reaction of polyhydroxyalkanoate which consists of a unit represented by chemical formula (32) synthesized in Example 5

[0216]

[chemical formula 67]



15

[0217]

0.50 g of a polyhydroxyalkanoate copolymer which consists of a unit represented by the chemical formula (32) (A: 14 mol%, B: 86 mol%) obtained in 20 Example 5 was added to an eggplant flask and dissolved with 30 ml of acetone added. This was placed in an ice bath, and 5 ml of acetic acid and

0.52 g of 18-crown-6-ether were added and the mixture was agitated. Next, 0.42 g of potassium permanganate was slowly added on the ice bath, and agitated in an ice bath for 2 hours, and agitated at room 5 temperature for further 18 hours. 60 ml of ethyl acetate was added after the reaction ended, and 45 ml of water was further added. Next, sodium hydrogen sulfite was added until peracid was removed. Then, the pH of the liquid was adjusted to 1 with 1.0 N 10 hydrochloric acid. The organic layer was extracted and washed 3 times with 1.0 N hydrochloric acid. After the organic layer was collected, crude polymer was collected by evaporating the solvent. Next, polymer was collected, after washed with 50 ml of 15 water, 50 ml of methanol and further with 50 ml of water 3 times. Next, it was dissolved in 3 ml of THF, re-precipitation was performed using methanol in an amount of 50 times of THF required for dissolving the polymer. The precipitation was collected and 0.43 g 20 of polymer was obtained by carrying out drying under reduced pressure.

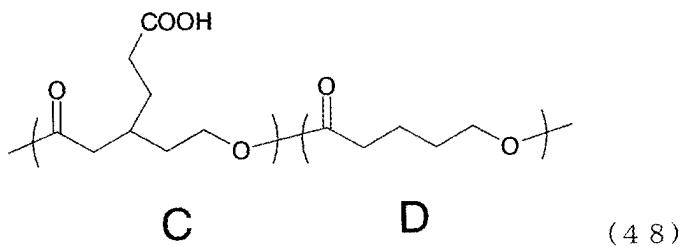
[0218]

In order to identify the structure of the obtained polymer, NMR analysis was performed on the 25 same conditions as in Example 1 and consequently it was confirmed that the obtained compound was a polyhydroxyalkanoate which contains a unit

represented by the following chemical formula (48) as a monomer unit.

[0219]

[chemical formula 68]



5

[0220]

The average molecular weight of the obtained polyhydroxyalkanoate was estimated by gel permeation chromatography (GPC; TOSOH HLC-8220, column; TOSOH 10 TSK-GEL Super HM-H, solvent; chloroform, polystyrene conversion). Consequently, the number average molecular weight, Mn was 17,900, and weight average molecular weight, Mw was 24,500.

[0221]

15 In order to calculate the unit of the obtained polyhydroxyalkanoate furthermore, carboxyl groups at the end of the side chains of the polyhydroxyalkanoate were subjected to methyl esterification using trimethylsilyldiazomethane and 20 the calculation was performed.

[0222]

30 mg of the target polyhydroxyalkanoate was

added to 100 ml-volume eggplant flask and dissolved with 2.1 ml of chloroform and 0.7 ml of methanol added. 0.5 ml of 2 mol/L trimethylsilyldiazomethane-hexane solution was added to this, and agitated at room temperature for 1 hour. After the reaction ended, the solvent was removed and the polymer was collected. It was washed with 50 ml of methanol and the polymer was collected after that. 29 mg of polyhydroxyalkanoate was obtained by carrying out drying under reduced pressure.

[0223]

NMR analysis was performed on the same conditions as in Example 1 and consequently it was confirmed that the obtained polyhydroxyalkanoate represented by the chemical formula (48) was a copolymer having a monomer ratio of 13 mol% for C unit and 87 mol% for D unit.

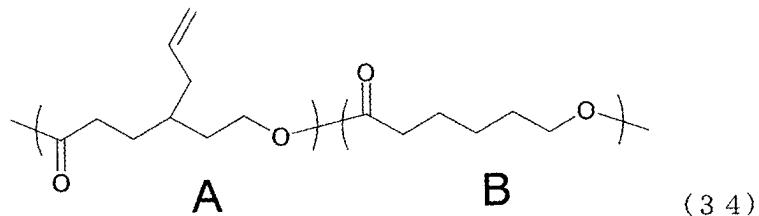
[0224]

(Example 15)

Oxidation reaction of polyhydroxyalkanoate which consists of a unit represented by chemical formula (34) synthesized in Example 6

[0225]

[chemical formula 69]



[0226]

0.50 g of a polyhydroxyalkanoate copolymer which consists of a unit represented by the chemical formula (34) (A: 13 mol%, B: 87 mol%) obtained in Example 6 was added to an eggplant flask and dissolved with 30 ml of acetone added. This was placed in an ice bath, and 5 ml of acetic acid and 0.43 g of 18-crown-6-ether were added and the mixture was agitated. Next, 0.34 g of potassium permanganate was slowly added on the ice bath, and agitated in an ice bath for 2 hours, and agitated at room temperature for further 18 hours. 60 ml of ethyl acetate was added after the reaction ended, and 45 ml of water was further added. Next, sodium hydrogen sulfite was added until peracid was removed. Then, the pH of the liquid was adjusted to 1 with 1.0 N hydrochloric acid. The organic layer was extracted and washed 3 times with 1.0 N hydrochloric acid. After the organic layer was collected, crude polymer was collected by evaporating the solvent. Next, polymer was collected, after washed with 50 ml of

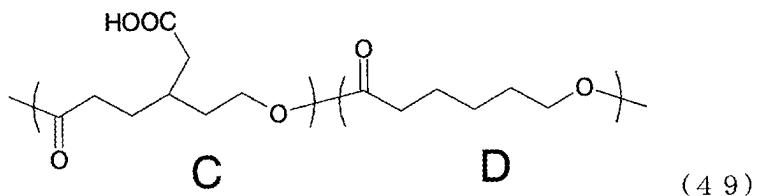
water, 50 ml of methanol and further with 50 ml of water 3 times. Next, it was dissolved in 3 ml of THF, re-precipitation was performed using methanol in an amount of 50 times of THF required for dissolving the polymer. The precipitation was collected and 0.44 g of polymer was obtained by carrying out drying under reduced pressure.

[0227]

In order to identify the structure of the obtained polymer, NMR analysis was performed on the same conditions as in Example 1 and consequently it was confirmed that the obtained compound was a polyhydroxyalkanoate which contains a unit represented by the following chemical formula (49) as a monomer unit.

[0228]

[chemical formula 70]



[0229]

The average molecular weight of the obtained polyhydroxyalkanoate was estimated by gel permeation chromatography (GPC; TOSOH HLC-8220, column; TOSOH

TSK-GEL Super HM-H, solvent; chloroform, polystyrene conversion). Consequently, the number average molecular weight, Mn was 18,900, and weight average molecular weight, Mw was 27,600.

5 [0230]

In order to calculate the unit of the obtained polyhydroxyalkanoate furthermore, carboxyl groups at the end of the side chains of the polyhydroxyalkanoate were subjected to methyl esterification using trimethylsilyldiazomethane and the calculation was performed.

10 [0231]

30 mg of the target polyhydroxyalkanoate was added to 100 ml-volume eggplant flask and dissolved with 2.1 ml of chloroform and 0.7 ml of methanol added. 0.5 ml of 2 mol/L trimethylsilyldiazomethane-hexane solution was added to this, and agitated at room temperature for 1 hour. After the reaction ended, the solvent was removed and the polymer was collected. It was washed with 50 ml of methanol and the polymer was collected after that. 28 mg of polyhydroxyalkanoate was obtained by carrying out drying under reduced pressure.

20 [0232]

25 NMR analysis was performed on the same conditions as in Example 1 and consequently it was confirmed that the obtained polyhydroxyalkanoate

represented by the chemical formula (49) was a copolymer having a monomer ratio of 12 mol% for C unit and 88 mol% for D unit.

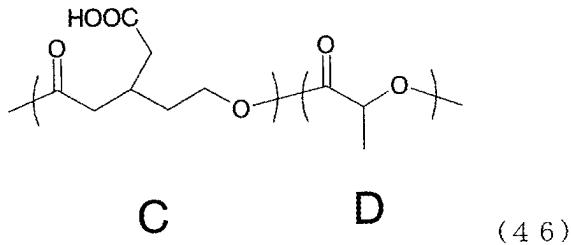
[0233]

5 (Example 16)

Condensation reaction of polyhydroxyalkanoate which consist of a unit represented by chemical formula (46) synthesized in Example 12 and 2-aminobenzenesulfonic acid

10 [0234]

[chemical formula 71]



[0235]

In a nitrogen atmosphere, 0.40 g of a polymer  
15 synthesized from the polyhydroxyalkanoate copolymer which consists of a unit represented by the chemical formula (46) (C: 8 mol%, D: 92 mol%) obtained in Example 12, 0.35 g of 2-aminobenzenesulfonic acid were added to a 100 ml three-necked flask and  
20 agitated with 15.0 ml of pyridine added, and then 1.06 ml of triphenyl phosphite was added and heated at 120°C for 6 hours. After the reaction ended, re-

precipitation was performed from 150 ml of ethanol to collect the product. The obtained polymer was washed with 1N hydrochloric acid for one day and further washed by agitating in water for one day, and 0.34 g 5 of polymer was obtained by carrying out drying under reduced pressure.

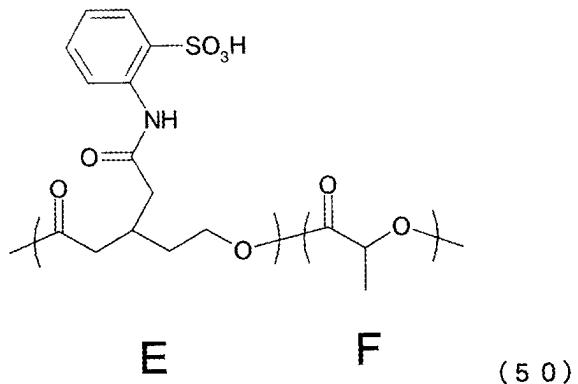
[0236]

The structure of the obtained polymer was determined by analyzing with  $^1\text{H-NMR}$  (FT-NMR: Bruker 10 DPX400; resonant frequency: 400 MHz; nuclide measured:  $^1\text{H}$ ; solvent used: d-DMSO; measurement temperature: room temperature) and Fourier transformation-infrared absorption (FT-IR) spectrum (Nicolet AVATAR360 FT-IR). As a result of performing 15 IR measurement, the peak of  $1,695 \text{ cm}^{-1}$  resulted from carboxylic acid decreased, and a peak resulted from amide group at  $1,658 \text{ cm}^{-1}$  was newly observed.

The results of  $^1\text{H-NMR}$  showed a shift of the peak resulted from the aromatic ring in 2- 20 aminobenzenesulfonic acid structure and accordingly it was confirmed that the obtained polymer was a polyhydroxyalkanoate containing a unit represented by the following chemical formula (50) as a monomer unit.

[0237]

25 [chemical formula 72]



[0238]

As for the ratio of the units in the polyhydroxyalkanoate represented by the chemical formula (50), it was confirmed that it was a copolymer having a monomer ratio of 8 mol% for unit E and 92 mol % for unit F.

[0239]

The average molecular weight of the obtained polyhydroxyalkanoate was estimated by gel permeation chromatography (GPC; TOSOH, column; Polymer Laboratories PLgel 5  $\mu$  MIXED-C, solvent; DMF/LiBr 0.1% (w/v), polystyrene conversion). Consequently, the number average molecular weight, Mn was 16,700, and weight average molecular weight, Mw was 24,700.

[0240]

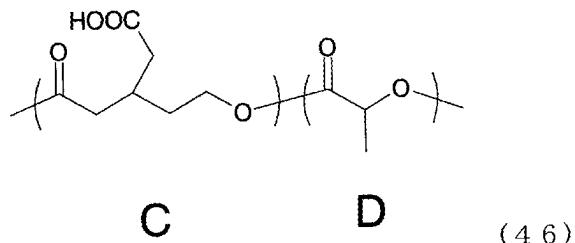
(Example 17)

Condensation reaction of polyhydroxyalkanoate which consist of a unit represented by chemical formula (46) synthesized in Example 12 and 4-

aminobenzenesulfonic acid

[0241]

[chemical formula 73]



5 [0242]

In a nitrogen atmosphere, 0.40 g of a polymer synthesized from the polyhydroxyalkanoate copolymer which consists of a unit represented by the chemical formula (46) (C: 8 mol%, D: 92 mol%) obtained in  
 10 Example 12, 0.35 g of 4-aminobenzenesulfonic acid were added to a 100 ml three-necked flask and agitated with 15.0 ml of pyridine added, and then 1.06 ml of triphenyl phosphite was added and heated at 120°C for 6 hours. After the reaction ended, re-  
 15 precipitation was performed from 150 ml of ethanol to collect the product. The obtained polymer was washed with 1N hydrochloric acid for one day and further washed by agitating in water for one day, and 0.32 g of polymer was obtained by carrying out drying under  
 20 reduced pressure.

[0243]

The structure of the obtained polymer was

determined by analyzing with  $^1\text{H-NMR}$  (FT-NMR: Bruker DPX400; resonant frequency: 400 MHz; nuclide measured:  $^1\text{H}$ ; solvent used: d-DMSO; measurement temperature: room temperature) and Fourier

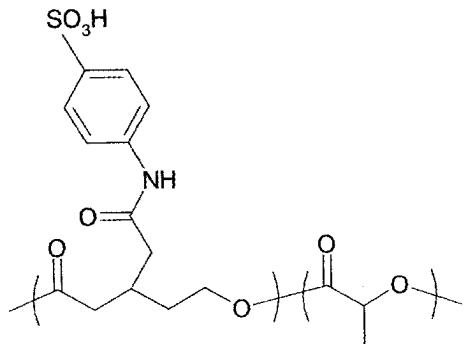
5 transformation-infrared absorption (FT-IR) spectrum (Nicolet AVATAR360 FT-IR). As a result of performing IR measurement, the peak of  $1,695 \text{ cm}^{-1}$  resulted from carboxylic acid decreased, and a peak resulted from amide group at  $1,658 \text{ cm}^{-1}$  was newly observed.

10 The results of  $^1\text{H-NMR}$  showed a shift of the peak resulted from the aromatic ring in 4-aminobenzenesulfonic acid structure and accordingly it was confirmed that the obtained polymer was a polyhydroxyalkanoate containing a unit represented by

15 the following chemical formula (51) as a monomer unit.

[0244]

[chemical formula 74]



E

F

(51)

[0245]

As for the ratio of the units in the polyhydroxyalkanoate represented by the chemical formula (51), it was confirmed that it was a copolymer having a monomer ratio of 8 mol% for unit E 5 and 92 mol % for unit F.

[0246]

The average molecular weight of the obtained polymer was estimated by gel permeation chromatography (GPC; TOSOH, column; Polymer 10 Laboratories PLgel 5  $\mu$  MIXED-C, solvent; DMF/LiBr 0.1% (w/v), polystyrene conversion). Consequently, the number average molecular weight, Mn was 16,100, and weight average molecular weight, Mw was 24,300.

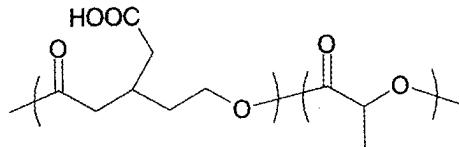
[0247]

15 (Example 18)

Condensation reaction of the polyhydroxyalkanoate which consist of a unit represented by chemical formula (46) synthesized in Example 12 and p-toluidine-2-sulfonic acid

20 [0248]

[chemical formula 75]



C

D

(46)

[0249]

In a nitrogen atmosphere, 0.40 g of a polymer synthesized from the polyhydroxyalkanoate copolymer which consists of a unit represented by the chemical formula (46) (C: 8 mol%, D: 92 mol%) obtained in Example 12, 0.38 g of p-toluidine-2-sulfonic acid were added to a 100 ml three-necked flask and agitated with 15.0 ml of pyridine added, and then 1.06 ml of triphenyl phosphite was added and heated at 120°C for 6 hours. After the reaction ended, reprecipitation was performed from 150 ml of ethanol to collect the product. The obtained polymer was washed with 1N hydrochloric acid for one day and further washed by agitating in water for one day, and 0.35 g of polymer was obtained by carrying out drying under reduced pressure.

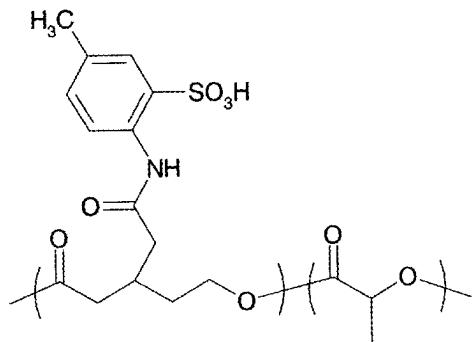
[0250]

The structure of the obtained polymer was determined by analyzing with  $^1\text{H-NMR}$  (FT-NMR: Bruker DPX400; resonant frequency: 400 MHz; nuclide measured:  $^1\text{H}$ ; solvent used: d-DMSO; measurement temperature: room temperature) and Fourier transformation-infrared absorption (FT-IR) spectrum (Nicolet AVATAR360 FT-IR). As a result of performing IR measurement, the peak of  $1,695 \text{ cm}^{-1}$  resulted from carboxylic acid decreased, and a peak resulted from amide group at  $1,658 \text{ cm}^{-1}$  was newly observed.

The results of  $^1\text{H-NMR}$  showed a shift of the peak resulted from the aromatic ring in p-toluidine-2-sulfonic acid structure and accordingly it was confirmed that the obtained polymer was a

- 5 polyhydroxyalkanoate containing a unit represented by the following chemical formula (52) as a monomer unit.  
 [0251]

[chemical formula 76]



E

F

(52)

- 10 [0252]

As for the ratio of the units in the polyhydroxyalkanoate represented by the chemical formula (52), it was confirmed that it was a copolymer having a monomer ratio of 8 mol% for unit E  
 15 and 92 mol % for unit F.

[0253]

The average molecular weight of the obtained polyhydroxyalkanoate was estimated by gel permeation chromatography (GPC; TOSOH, column; Polymer

Laboratories PLgel 5  $\mu$  MIXED-C, solvent; DMF/LiBr 0.1% (w/v), polystyrene conversion). Consequently, the number average molecular weight, Mn was 15,700, and weight average molecular weight, Mw was 24,600.

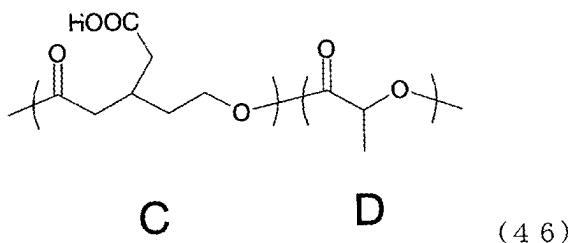
5 [0254]

(Example 19)

Condensation reaction of polyhydroxyalkanoate which consist of a unit represented by chemical formula (46) synthesized in Example 12 and 2-  
10 aminobenzenesulfonic acid phenyl ester

[0255]

[chemical formula 77]



[0256]

15 In a nitrogen atmosphere, 0.40 g of a polymer synthesized from the polyhydroxyalkanoate copolymer which consists of a unit represented by the chemical formula (46) (C: 8 mol%, D: 92 mol%) obtained in Example 12, 0.51 g of 2-aminobenzenesulfonic acid  
20 phenyl ester were added to a 100 ml three-necked flask and agitated with 15.0 ml of pyridine added, and then 1.06 ml of triphenyl phosphite was added and

heated at 120°C for 6 hours. After the reaction ended, re-precipitation was performed from 150 ml of ethanol to collect the product. The obtained polymer was washed with 1N hydrochloric acid for one day and 5 further washed by agitating in water for one day, and 0.38 g of polymer was obtained by carrying out drying under reduced pressure.

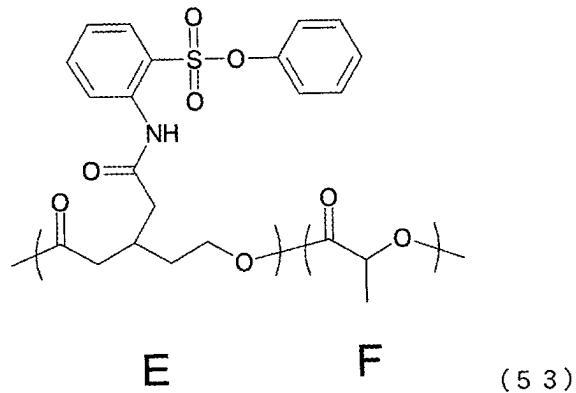
[0257]

The structure of the obtained polymer was 10 determined by analyzing with  $^1\text{H}$ -NMR (FT-NMR: Bruker DPX400; resonant frequency: 400 MHz; nuclide measured:  $^1\text{H}$ ; solvent used: d-DMSO; measurement temperature: room temperature) and Fourier transformation-infrared absorption (FT-IR) spectrum 15 (Nicolet AVATAR360 FT-IR). As a result of performing IR measurement, the peak of  $1,695 \text{ cm}^{-1}$  resulted from carboxylic acid decreased, and a peak resulted from amide group at  $1,658 \text{ cm}^{-1}$  was newly observed.

The results of  $^1\text{H}$ -NMR showed a shift of the 20 peak resulted from the aromatic ring in 2-aminobenzenesulfonic acid phenyl ester structure and accordingly it was confirmed that the obtained polymer was a polyhydroxyalkanoate containing a unit represented by the following chemical formula (53) as 25 a monomer unit.

[0258]

[chemical formula 78]



[0259]

As for the ratio of the units in the polyhydroxyalkanoate represented by the chemical formula (53), it was confirmed that it was a copolymer having a monomer ratio of 8 mol% for unit E and 92 mol % for unit F.

[0260]

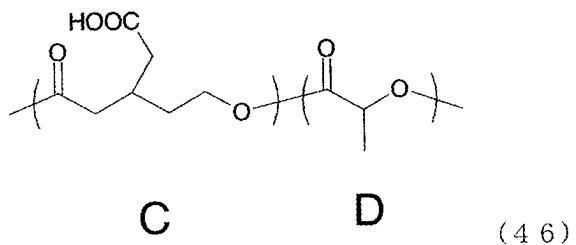
The average molecular weight of the obtained polyhydroxyalkanoate was estimated by gel permeation chromatography (GPC; TOSOH, column; Polymer Laboratories PLgel 5  $\mu$  MIXED-C, solvent; DMF/LiBr 0.1% (w/v), polystyrene conversion). Consequently, the number average molecular weight, Mn was 17,100, and weight average molecular weight, Mw was 24,600.

[0261]

(Example 20)

Condensation reaction of the polyhydroxyalkanoate which consist of a unit

represented by chemical formula (46) synthesized in Example 12 and 2-amino-1-naphthalenesulfonic acid [0262] [chemical formula 79]



5

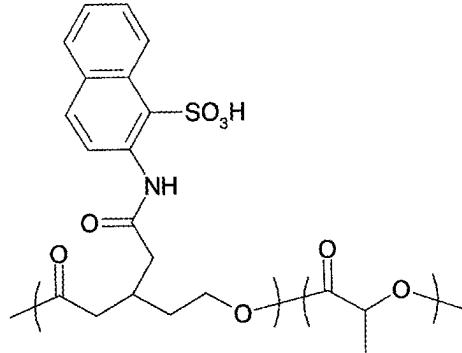
[0263]

In a nitrogen atmosphere, 0.40 g of a polymer synthesized from the polyhydroxyalkanoate copolymer which consists of a unit represented by the chemical formula (46) (C: 8 mol%, D: 92 mol%) obtained in Example 12, 0.45 g of 2-amino-1-naphthalenesulfonic acid were added to a 100 ml three-necked flask and agitated with 15.0 ml of pyridine added, and then 1.06 ml of triphenyl phosphite was added and heated at 120°C for 6 hours. After the reaction ended, reprecipitation was performed from 150 ml of ethanol to collect the product. The obtained polymer was washed with 1N hydrochloric acid for one day and further washed by agitating in water for one day, and 0.34 g of polymer was obtained by carrying out drying under reduced pressure.

[0264]

The structure of the obtained polymer was determined by analyzing with  $^1\text{H-NMR}$  (FT-NMR: Bruker DPX400; resonant frequency: 400 MHz; nuclide measured:  $^1\text{H}$ ; solvent used: d-DMSO; measurement 5 temperature: room temperature) and Fourier transformation-infrared absorption (FT-IR) spectrum (Nicolet AVATAR360 FT-IR). As a result of performing IR measurement, the peak of  $1,695 \text{ cm}^{-1}$  resulted from carboxylic acid decreased, and a peak resulted from 10 amide group at  $1,658 \text{ cm}^{-1}$  was newly observed.

The results of  $^1\text{H-NMR}$  showed a shift of the peak resulted from the aromatic ring in 2-amino-1-naphthalenesulfonic acid structure and accordingly it was confirmed that the obtained polymer was a 15 polyhydroxyalkanoate containing a unit represented by the following chemical formula (54) as a monomer unit.  
[0265]  
[chemical formula 80]



E

F

(54)

[0266]

As for the ratio of the units in the polyhydroxyalkanoate represented by the chemical formula (54), it was confirmed that it was a 5 copolymer having a monomer ratio of 8 mol% for unit E and 92 mol % for unit F.

[0267]

The average molecular weight of the obtained polyhydroxyalkanoate was estimated by gel permeation 10 chromatography (GPC; TOSOH, column; Polymer Laboratories PLgel 5  $\mu$  MIXED-C, solvent; DMF/LiBr 0.1% (w/v), polystyrene conversion). Consequently, the number average molecular weight, Mn was 16,900, and weight average molecular weight, Mw was 25,700.

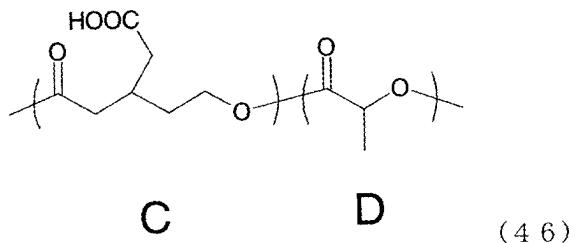
15 [0268]

(Example 21)

Condensation reaction of the polyhydroxyalkanoate which consist of a unit 20 represented by chemical formula (46) synthesized in Example 12 and 2-amino-2-methylpropanesulfonic acid

[0269]

[chemical formula 81]



[0270]

In a nitrogen atmosphere, 0.40 g of a polymer synthesized from the polyhydroxyalkanoate copolymer 5 which consists of a unit represented by the chemical formula (46) (C: 8 mol%, D: 92 mol%) obtained in Example 12, 0.31 g of 2-amino-2-methylpropanesulfonic acid were added to a 100 ml three-necked flask and agitated with 15.0 ml of pyridine added, and then 10 1.06 ml of triphenyl phosphite was added and heated at 120°C for 6 hours. After the reaction ended, re-precipitation was performed from 150 ml of ethanol to collect the product. The obtained polymer was washed with 1N hydrochloric acid for one day and further 15 washed by agitating in water for one day, and 0.31 g of polymer was obtained by carrying out drying under reduced pressure.

[0271]

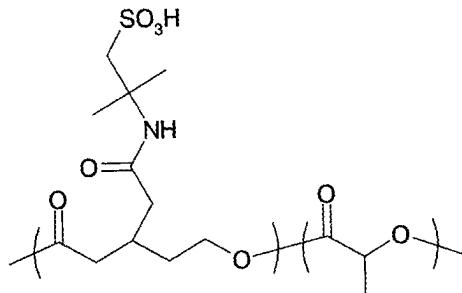
The structure of the obtained polymer was 20 determined by analyzing with  $^1\text{H}$ -NMR (FT-NMR: Bruker DPX400; resonant frequency: 400 MHz; nuclide measured:  $^1\text{H}$ ; solvent used: d-DMSO; measurement

temperature: room temperature) and Fourier transformation-infrared absorption (FT-IR) spectrum (Nicolet AVATAR360 FT-IR). As a result of performing IR measurement, the peak of  $1,695\text{ cm}^{-1}$  resulted from 5 carboxylic acid decreased, and a peak resulted from amide group at  $1,668\text{ cm}^{-1}$  was newly observed.

The results of  $^1\text{H-NMR}$  showed a shift of the peak resulted from the methylene of 2-amino-2-methylpropanesulfonic acid structure and accordingly 10 it was confirmed that the obtained polymer was a polyhydroxyalkanoate containing a unit represented by the following chemical formula (55) as a monomer unit.

[0272]

[chemical formula 82]



E

F

(55)

15

[0273]

As for the ratio of the units in the polyhydroxyalkanoate represented by the chemical formula (55), it was confirmed that it was a 20 copolymer having a monomer ratio of 8 mol% for unit E

and 92 mol% for unit F.

[0274]

The average molecular weight of the obtained polyhydroxyalkanoate was estimated by gel permeation chromatography (GPC; TOSOH, column; Polymer Laboratories PLgel 5  $\mu$  MIXED-C, solvent; DMF/LiBr 0.1% (w/v), polystyrene conversion). Consequently, the number average molecular weight, Mn was 17,300, and weight average molecular weight, Mw was 24,600.

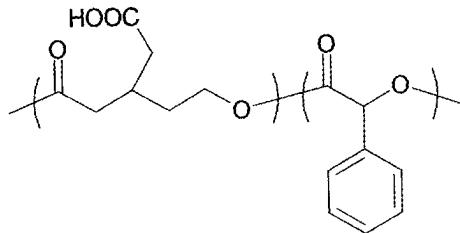
10 [0275]

(Example 22)

Condensation reaction of polyhydroxyalkanoate which consist of a unit represented by chemical formula (47) synthesized in Example 13 and 3-15 aminobenzenesulfonic acid

[0276]

[chemical formula 83]



C

D

(47)

[0277]

20 In a nitrogen atmosphere, 0.40 g of a polymer synthesized from the polyhydroxyalkanoate copolymer

which consists of a unit represented by the chemical formula (47) (C: 10 mol%, D: 90 mol%) obtained in Example 13, 0.25 g of 3-aminobenzenesulfonic acid were added to a 100 ml three-necked flask and  
5 agitated with 15.0 ml of pyridine added, and then 0.76 ml of triphenyl phosphite was added and heated at 120°C for 6 hours. After the reaction ended, re-precipitation was performed from 150 ml of ethanol to collect the product. The obtained polymer was washed  
10 with 1N hydrochloric acid for one day and further washed by agitating in water for one day, and 0.33 g of polymer was obtained by carrying out drying under reduced pressure.

[0278]

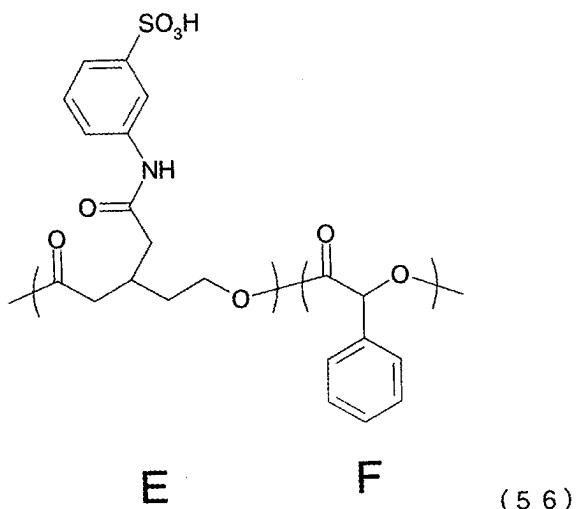
15 The structure of the obtained polymer was determined by analyzing with  $^1\text{H-NMR}$  (FT-NMR: Bruker DPX400; resonant frequency: 400 MHz; nuclide measured:  $^1\text{H}$ ; solvent used: d-DMSO; measurement temperature: room temperature) and Fourier  
20 transformation-infrared absorption (FT-IR) spectrum (Nicolet AVATAR360 FT-IR). As a result of performing IR measurement, the peak of  $1,695 \text{ cm}^{-1}$  resulted from carboxylic acid decreased, and a peak resulted from amide group at  $1,658 \text{ cm}^{-1}$  was newly observed.

25 The results of  $^1\text{H-NMR}$  showed a shift of the peak resulted from the aromatic ring of 3-aminobenzenesulfonic acid structure and accordingly

it was confirmed that the obtained polymer was a polyhydroxyalkanoate containing a unit represented by the following chemical formula (56) as a monomer unit.

[0279]

5 [chemical formula 84]



[0280]

As for the ratio of the units in the polyhydroxyalkanoate represented by the chemical formula (56), it was confirmed that it was a copolymer having a monomer ratio of 10 mol% for unit E and 90 mol% for unit F.

[0281]

The average molecular weight of the obtained polyhydroxyalkanoate was estimated by gel permeation chromatography (GPC; TOSOH, column; Polymer Laboratories PLgel 5  $\mu$  MIXED-C, solvent; DMF/LiBr 0.1% (w/v), polystyrene conversion). Consequently,

the number average molecular weight, Mn was 13,100, and weight average molecular weight, Mw was 17,700.

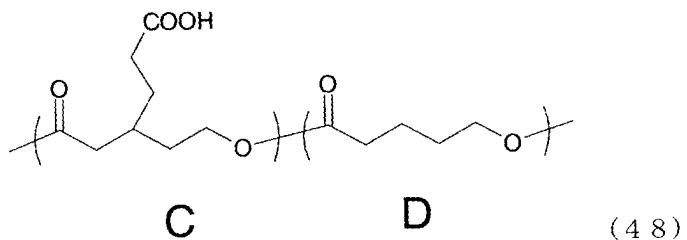
[0282]

(Example 23)

5 Condensation reaction of the polyhydroxyalkanoate which consist of a unit represented by chemical formula (48) synthesized in Example 14 and 4-methoxyaniline-2-sulfonic acid

[0283]

10 [chemical formula 85]



[0284]

In a nitrogen atmosphere, 0.40 g of a polymer synthesized from the polyhydroxyalkanoate copolymer  
 15 which consists of a unit represented by the chemical formula (48) (C: 13 mol%, D: 87 mol%) obtained in Example 14, 0.48g of 4-methoxyaniline-2-sulfonic acid were added to a 100 ml three-necked flask and agitated with 15.0 ml of pyridine added, and then 20 1.24 ml of triphenyl phosphite was added and heated at 120°C for 6 hours. After the reaction ended, re-precipitation was performed from 150 ml of ethanol to

collect the product. The obtained polymer was washed with 1N hydrochloric acid for one day and further washed by agitating in water for one day, and 0.37 g of polymer was obtained by carrying out drying under 5 reduced pressure.

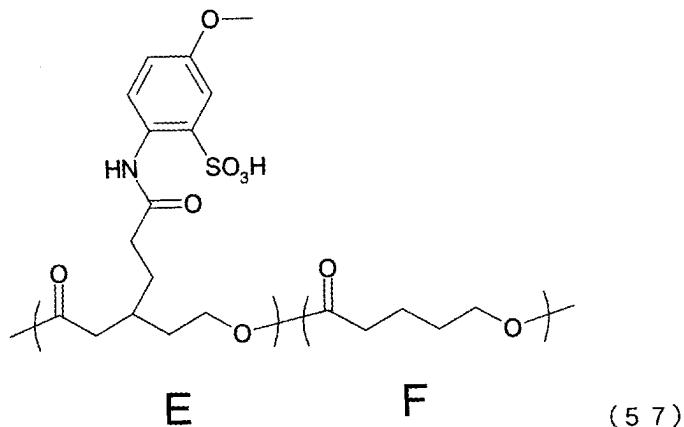
[0285]

The structure of the obtained polymer was determined by analyzing with  $^1\text{H}$ -NMR (FT-NMR: Bruker DPX400; resonant frequency: 400 MHz; nuclide 10 measured:  $^1\text{H}$ ; solvent used: d-DMSO; measurement temperature: room temperature) and Fourier transformation-infrared absorption (FT-IR) spectrum (Nicolet AVATAR360 FT-IR). As a result of performing IR measurement, the peak of  $1,695 \text{ cm}^{-1}$  resulted from 15 carboxylic acid decreased, and a peak resulted from amide group at  $1,658 \text{ cm}^{-1}$  was newly observed.

The results of  $^1\text{H}$ -NMR showed a shift of the peak resulted from the aromatic ring of 4-methoxyaniline-2-sulfonic acid structure and 20 accordingly it was confirmed that the obtained polymer was a polyhydroxyalkanoate containing a unit represented by the following chemical formula (57) as a monomer unit.

[0286]

25 [chemical formula 86]



[0287]

As for the ratio of the units in the polyhydroxyalkanoate represented by the chemical formula (57), it was confirmed that it was a copolymer having a monomer ratio of 13 mol% for unit E and 87 mol% for unit F.

[0288]

The average molecular weight of the obtained polymer was estimated by gel permeation chromatography (GPC; TOSOH, column; Polymer Laboratories PLgel 5  $\mu$  MIXED-C, solvent; DMF/LiBr 0.1% (w/v), polystyrene conversion). Consequently, the number average molecular weight, Mn was 14,800, and weight average molecular weight, Mw was 20,600.

[0289]

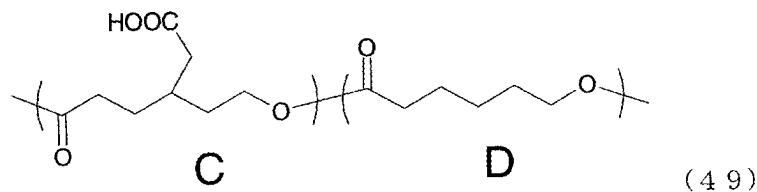
(Example 24)

Condensation reaction of the polyhydroxyalkanoate which consist of a unit

represented by chemical formula (49) synthesized in Example 15 and taurine

[0290]

[chemical formula 87]



5

[0291]

In a nitrogen atmosphere, 0.40 g of a polymer synthesized from the polyhydroxyalkanoate copolymer which consists of a unit represented by the chemical formula (49) (C: 12 mol%, D: 88 mol%) obtained in Example 15, 0.25 g of taurine were added to a 100 ml three-necked flask and agitated with 15.0 ml of pyridine added, and then 1.03 ml of triphenyl phosphite was added and heated at 120°C for 6 hours.

10 After the reaction ended, re-precipitation was performed from 150 ml of ethanol to collect the product. The obtained polymer was washed with 1N hydrochloric acid for one day and further washed by agitating in water for one day, and 0.31 g of polymer

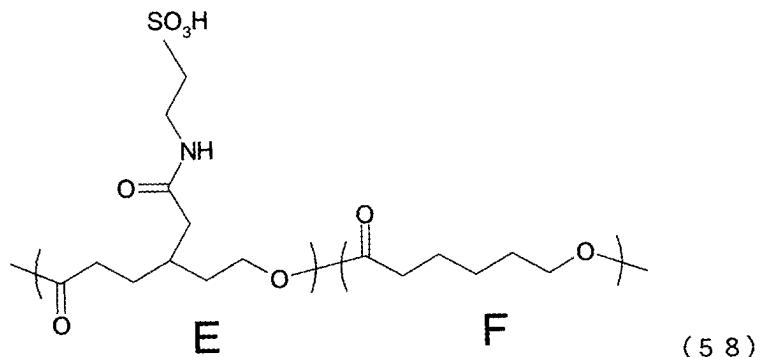
15 was obtained by carrying out drying under reduced pressure.

20 [0292]

The structure of the obtained polymer was

determined by analyzing with  $^1\text{H-NMR}$  (FT-NMR: Bruker DPX400; resonant frequency: 400 MHz; nuclide measured:  $^1\text{H}$ ; solvent used: d-DMSO; measurement temperature: room temperature) and Fourier transformation-infrared absorption (FT-IR) spectrum (Nicolet AVATAR360 FT-IR). As a result of performing IR measurement, the peak of  $1,695 \text{ cm}^{-1}$  resulted from carboxylic acid decreased, and a peak resulted from amide group at  $1,668 \text{ cm}^{-1}$  was newly observed.

[0293]  
[chemical formula 88]



[0294]  
20 As for the ratio of the units in the  
polyhydroxalkanoate represented by the chemical

formula (58), it was confirmed that it was a copolymer having a monomer ratio of 12 mol% for unit E and 88 mol% for unit F.

[0295]

5 The average molecular weight of the obtained polymer was estimated by gel permeation chromatography (GPC; TOSOH, column; Polymer Laboratories PLgel 5  $\mu$  MIXED-C, solvent; DMF/LiBr 0.1% (w/v), polystyrene conversion). Consequently, 10 the number average molecular weight, Mn was 15,500, and weight average molecular weight, Mw was 22,200.

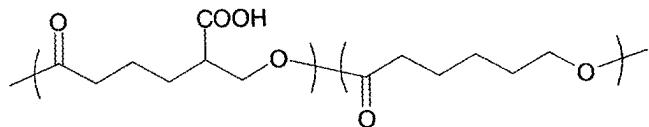
[0296]

(Example 25)

Condensation reaction of polyhydroxyalkanoate 15 which consist of a unit represented by chemical formula (37) synthesized in Example 7 and 2-aminobenzenesulfonic acid

[0297]

[chemical formula 89]



C

D

(37)

20

[0298]

In a nitrogen atmosphere, 0.40 g of a polymer

synthesized from the polyhydroxyalkanoate copolymer which consists of a unit represented by the chemical formula (37) (C: 14 mol%, D: 86 mol%) obtained in Example 7, 0.40 g of 2-aminobenzenesulfonic acid were 5 added to a 100 ml three-necked flask and agitated with 15.0 ml of pyridine added, and then 1.21 ml of triphenyl phosphite was added and heated at 120°C for 6 hours. After the reaction ended, re-precipitation was performed from 150 ml of ethanol to collect the 10 product. The obtained polymer was washed with 1N hydrochloric acid for one day and further washed by agitating in water for one day, and 0.36 g of polymer was obtained by carrying out drying under reduced pressure.

15 [0299]

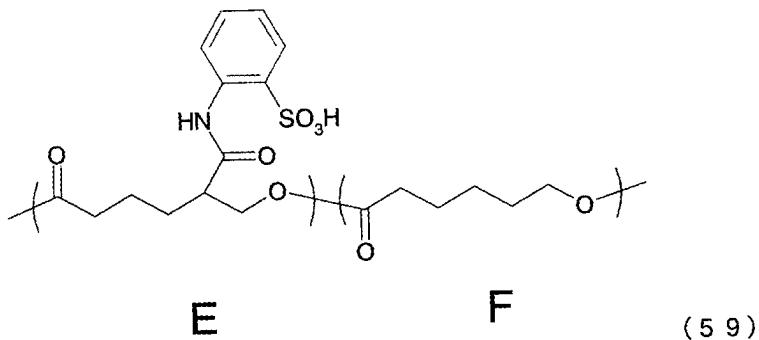
The structure of the obtained polymer was determined by analyzing with  $^1\text{H-NMR}$  (FT-NMR: Bruker DPX400; resonant frequency: 400 MHz; nuclide measured:  $^1\text{H}$ ; solvent used: d-DMSO; measurement 20 temperature: room temperature) and Fourier transformation-infrared absorption (FT-IR) spectrum (Nicolet AVATAR360 FT-IR). As a result of performing IR measurement, the peak of  $1,695 \text{ cm}^{-1}$  resulted from carboxylic acid decreased, and a peak resulted from 25 amide group at  $1,658 \text{ cm}^{-1}$  was newly observed.

The results of  $^1\text{H-NMR}$  showed a shift of the peak resulted from the aromatic ring of 2-

aminobenzenesulfonic acid structure and accordingly it was confirmed that the obtained polymer was a polyhydroxyalkanoate containing a unit represented by the following chemical formula (59) as a monomer unit.

5 [0300]

[chemical formula 90]



[0301]

As for the ratio of the units in the  
10 polyhydroxyalkanoate represented by the chemical formula (59), it was confirmed that it was a copolymer having a monomer ratio of 14 mol% for unit E and 86 mol% for unit F.

[0302]

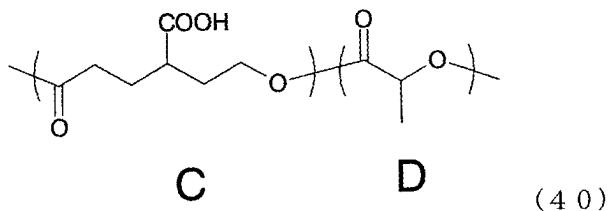
15 The average molecular weight of the obtained polymer was estimated by gel permeation chromatography (GPC; TOSOH, column; Polymer Laboratories PLgel 5  $\mu$  MIXED-C, solvent; DMF/LiBr 0.1% (w/v), polystyrene conversion). Consequently,  
20 the number average molecular weight, Mn was 9,400, and weight average molecular weight, Mw was 13,400.

[0303]

(Example 26)

Condensation reaction of the polyhydroxyalkanoate which consist of a unit represented by chemical formula (40) synthesized in Example 8 and 2-amino-2-methylpropanesulfonic acid [0304]

[chemical formula 91]



10 [0305]

In a nitrogen atmosphere, 0.40 g of a polymer synthesized from the polyhydroxyalkanoate copolymer which consists of a unit represented by the chemical formula (40) (C: 8 mol%, D: 92 mol%) obtained in Example 8, 0.31 g of 2-amino-2-methylpropanesulfonic acid were added to a 100 ml three-necked flask and agitated with 15.0 ml of pyridine added, and then 1.06 ml of triphenyl phosphite was added and heated at 120°C for 6 hours. After the reaction ended, re-precipitation was performed from 150 ml of ethanol to collect the product. The obtained polymer was washed with 1N hydrochloric acid for one day and further washed by agitating in water for one day, and 0.33 g

of polymer was obtained by carrying out drying under reduced pressure.

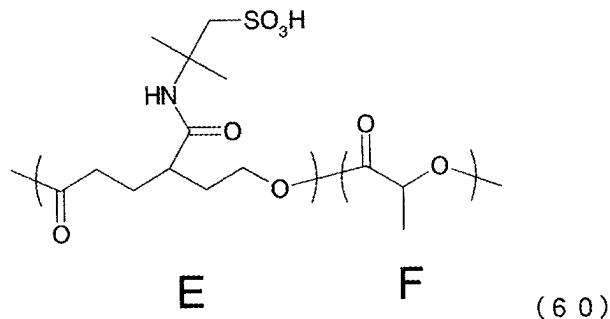
[0306]

The structure of the obtained polymer was  
5 determined by analyzing with  $^1\text{H-NMR}$  (FT-NMR: Bruker DPX400; resonant frequency: 400 MHz; nuclide measured:  $^1\text{H}$ ; solvent used: d-DMSO; measurement temperature: room temperature) and Fourier transformation-infrared absorption (FT-IR) spectrum  
10 (Nicolet AVATAR360 FT-IR). As a result of performing IR measurement, the peak of  $1,695 \text{ cm}^{-1}$  resulted from carboxylic acid decreased, and a peak resulted from amide group at  $1,668 \text{ cm}^{-1}$  was newly observed.

The results of  $^1\text{H-NMR}$  showed a shift of the  
15 peak resulted from the aromatic ring of 2-amino-2-methylpropanesulfonic acid structure and accordingly it was confirmed that the obtained polymer was a polyhydroxyalkanoate containing a unit represented by the following chemical formula (60) as a monomer unit.

20 [0307]

[chemical formula 92]



[0308]

As for the ratio of the units in the polyhydroxyalkanoate represented by the chemical formula (60), it was confirmed that it was a copolymer having a monomer ratio of 8 mol% for unit E and 92 mol% for unit F.

[0309]

The average molecular weight of the obtained polymer was estimated by gel permeation chromatography (GPC; TOSOH, column; Polymer Laboratories PLgel 5  $\mu$  MIXED-C, solvent; DMF/LiBr 0.1% (w/v), polystyrene conversion). Consequently, the number average molecular weight, Mn was 8,100, and weight average molecular weight, Mw was 12,400.

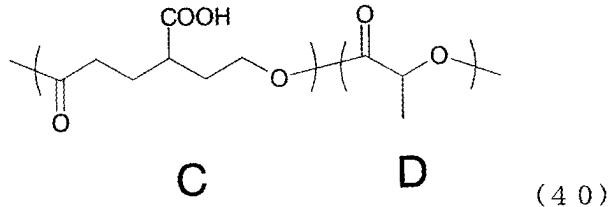
[0310]

(Example 27)

Condensation reaction of polyhydroxyalkanoate which consist of a unit represented by chemical formula (40) synthesized in Example 8 and 4-aminobenzenesulfonic acid phenyl ester

[0311]

[chemical formula 93]



[0312]

5         In a nitrogen atmosphere, 0.40 g of a polymer synthesized from the polyhydroxyalkanoate copolymer which consists of a unit represented by the chemical formula (40) (C: 8 mol%, D: 92 mol%) obtained in Example 8, 0.51 g of 4-aminobenzenesulfonic acid phenyl ester were added to a 100 ml three-necked flask and agitated with 15.0 ml of pyridine added, and then 1.06 ml of triphenyl phosphite was added and heated at 120°C for 6 hours. After the reaction ended, re-precipitation was performed from 150 ml of ethanol to collect the product. The obtained polymer was washed with 1N hydrochloric acid for one day and further washed by agitating in water for one day, and 0.35 g of polymer was obtained by carrying out drying under reduced pressure.

10         15         20         [0313]

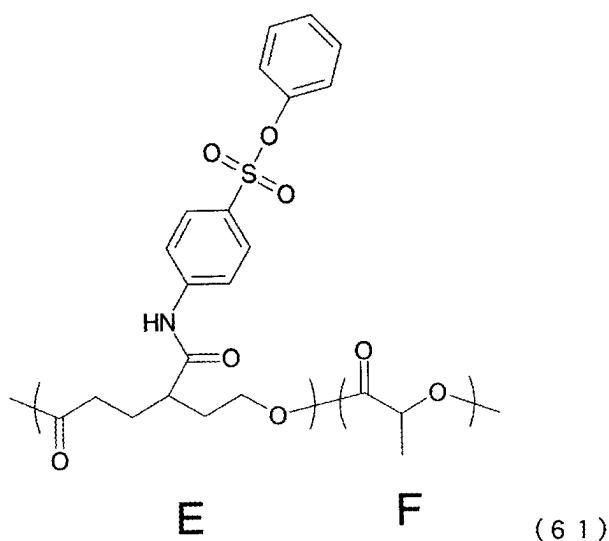
The structure of the obtained polymer was determined by analyzing with  $^1\text{H-NMR}$  (FT-NMR: Bruker DPX400; resonant frequency: 400 MHz; nuclide

measured:  $^1\text{H}$ ; solvent used: d-DMSO; measurement temperature: room temperature) and Fourier transformation-infrared absorption (FT-IR) spectrum (Nicolet AVATAR360 FT-IR). As a result of performing 5 IR measurement, the peak of  $1,695 \text{ cm}^{-1}$  resulted from carboxylic acid decreased, and a peak resulted from amide group at  $1,658 \text{ cm}^{-1}$  was newly observed.

The results of  $^1\text{H-NMR}$  showed a shift of the peak resulted from the aromatic ring of 4-10 aminobenzenesulfonic acid phenyl ester structure and accordingly it was confirmed that the obtained polymer was a polyhydroxyalkanoate containing a unit represented by the following chemical formula (61) as a monomer unit.

15 [0314]

[chemical formula 94]



[0315]

As for the ratio of the units in the polyhydroxyalkanoate represented by the chemical formula (61), it was confirmed that it was a 5 copolymer having a monomer ratio of 8 mol% for unit E and 92 mol% for unit F.

[0316]

The average molecular weight of the obtained polyhydroxyalkanoate was estimated by gel permeation 10 chromatography (GPC; TOSOH, column; Polymer Laboratories PLgel 5  $\mu$  MIXED-C, solvent; DMF/LiBr 0.1% (w/v), polystyrene conversion). Consequently, the number average molecular weight, Mn was 7,800, and weight average molecular weight, Mw was 14,300.

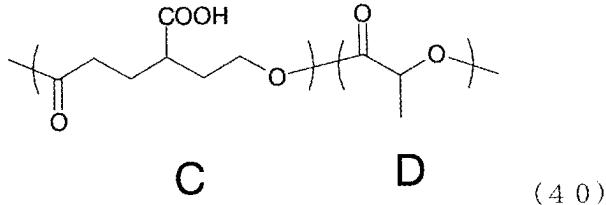
15 [0317]

(Example 28)

Condensation reaction of the polyhydroxyalkanoate which consist of a unit 20 represented by chemical formula (40) synthesized in Example 8 and 1-naphthylamine-8-sulfonic acid

[0318]

[chemical formula 95]



[0319]

In a nitrogen atmosphere, 0.40 g of a polymer synthesized from the polyhydroxyalkanoate copolymer which consists of a unit represented by the chemical formula (40) (C: 8 mol%, D: 92 mol%) obtained in Example 8, 0.45 g of 1-naphthylamine-8-sulfonic acid were added to a 100 ml three-necked flask and agitated with 15.0 ml of pyridine added, and then 1.06 ml of triphenyl phosphite was added and heated at 120°C for 6 hours. After the reaction ended, reprecipitation was performed from 150 ml of ethanol to collect the product. The obtained polymer was washed with 1N hydrochloric acid for one day and further washed by agitating in water for one day, and 0.33 g of polymer was obtained by carrying out drying under reduced pressure.

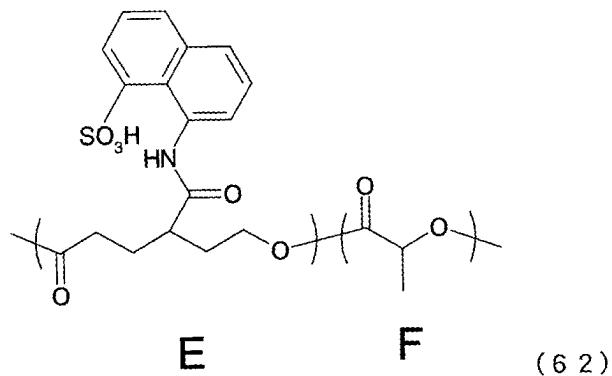
[0320]

The structure of the obtained polymer was determined by analyzing with  $^1\text{H-NMR}$  (FT-NMR: Bruker DPX400; resonant frequency: 400 MHz; nuclide measured:  $^1\text{H}$ ; solvent used: d-DMSO; measurement temperature: room temperature) and Fourier transformation-infrared absorption (FT-IR) spectrum (Nicolet AVATAR360 FT-IR). As a result of performing IR measurement, the peak of  $1,695 \text{ cm}^{-1}$  resulted from carboxylic acid decreased, and a peak resulted from amide group at  $1,658 \text{ cm}^{-1}$  was newly observed.

The results of  $^1\text{H-NMR}$  showed a shift of the peak resulted from the aromatic ring of 1-naphthylamine-8-sulfonic acid structure and accordingly it was confirmed that the obtained 5 polymer was a polyhydroxyalkanoate containing a unit represented by the following chemical formula (62) as a monomer unit.

[0321]

[chemical formula 96]



10

[0322]

As for the ratio of the units in the polyhydroxyalkanoate represented by the chemical formula (62), it was confirmed that it was a 15 copolymer having a monomer ratio of 8 mol% for unit E and 92 mol% for unit F.

[0323]

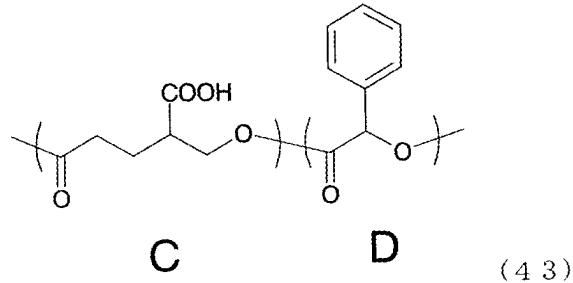
The average molecular weight of the obtained polymer was estimated by gel permeation 20 chromatography (GPC; TOSOH, column; Polymer

Laboratories PLgel 5  $\mu$  MIXED-C, solvent; DMF/LiBr 0.1% (w/v), polystyrene conversion). Consequently, the number average molecular weight, Mn was 8,200, and weight average molecular weight, Mw was 12,400.

5 [0324]

(Example 29)

Condensation reaction of the polyhydroxyalkanoate which consist of a unit represented by chemical formula (43) synthesized in  
 10 Example 9 and 4-methoxyaniline-2-sulfonic acid  
 [0325]  
 [chemical formula 97]



[0326]

15 In a nitrogen atmosphere, 0.40 g of a polymer synthesized from the polyhydroxyalkanoate copolymer which consists of a unit represented by the chemical formula (43) (C: 7 mol%, D: 93 mol%) obtained in Example 9, 0.21 g of 4-methoxyaniline-2-sulfonic acid  
 20 were added to a 100 ml three-necked flask and agitated with 15.0 ml of pyridine added, and then 0.54 ml of triphenyl phosphite was added and heated

at 120°C for 6 hours. After the reaction ended, re-precipitation was performed from 150 ml of ethanol to collect the product. The obtained polymer was washed with 1N hydrochloric acid for one day and further 5 washed by agitating in water for one day, and 0.32 g of polymer was obtained by carrying out drying under reduced pressure.

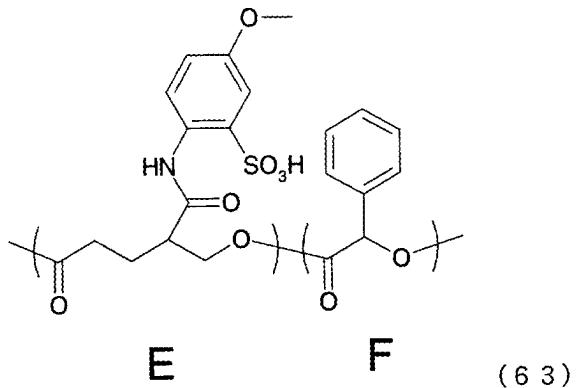
[0327]

The structure of the obtained polymer was 10 determined by analyzing with  $^1\text{H-NMR}$  (FT-NMR: Bruker DPX400; resonant frequency: 400 MHz; nuclide measured:  $^1\text{H}$ ; solvent used: d-DMSO; measurement temperature: room temperature) and Fourier transformation-infrared absorption (FT-IR) spectrum 15 (Nicolet AVATAR360 FT-IR). As a result of performing IR measurement, the peak of  $1,695 \text{ cm}^{-1}$  resulted from carboxylic acid decreased, and a peak resulted from amide group at  $1,658 \text{ cm}^{-1}$  was newly observed.

The results of  $^1\text{H-NMR}$  showed a shift of the 20 peak resulted from the aromatic ring of 4-methoxyaniline-2-sulfonic acid structure and accordingly it was confirmed that the obtained polymer was a polyhydroxyalkanoate containing a unit represented by the following chemical formula (63) as 25 a monomer unit.

[0328]

[chemical formula 98]



[0329]

As for the ratio of the units in the polyhydroxyalkanoate represented by the chemical formula (63), it was confirmed that it was a copolymer having a monomer ratio of 7 mol% for unit E and 93 mol% for unit F.

[0330]

The average molecular weight of the obtained polymer was estimated by gel permeation chromatography (GPC; TOSOH, column; Polymer Laboratories PLgel 5  $\mu$  MIXED-C, solvent; DMF/LiBr 0.1% (w/v), polystyrene conversion). Consequently, the number average molecular weight, Mn was 6,900, and weight average molecular weight, Mw was 10,100.

[0331]

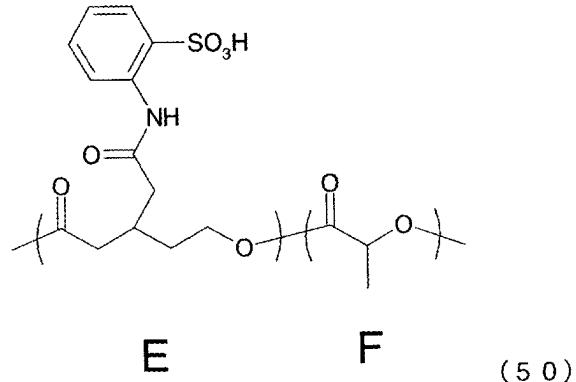
(Example 30)

Esterification reaction of the polyhydroxyalkanoate which consists of a unit represented by chemical formula (50) synthesized in

## Example 16

[0332]

[chemical formula 99]



5 [0333]

0.30 g of the polyhydroxyalkanoate copolymer which consists of a unit represented by the chemical formula (50) (E: 8 mol%, F: 92 mol%) obtained in Example 16 was added to an eggplant flask and dissolved with 21.0 ml of chloroform and 7.0 ml of methanol added and cooled to 0°C. 1.31 ml of 2 mol/L trimethylsilyldiazomethane-hexane solution (product of Aldrich) was added to this, and agitated for 4 hours. After the reaction ended, the solvent was removed with an evaporator and the polymer was collected.

15 [0334]

21.0 ml of chloroform, 7.0 ml of methanol were further added to re-dissolve the polymer and the solvent was evaporated by an evaporator. This

operation was repeated 3 times.

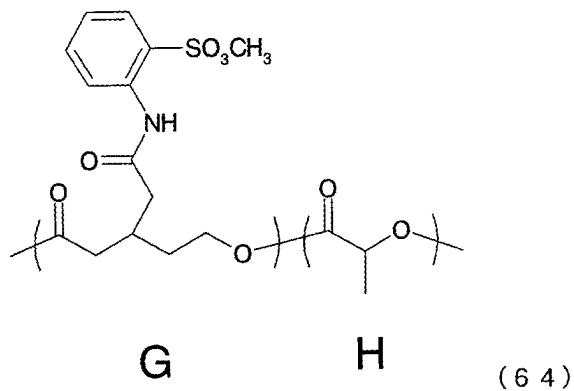
[0335]

0.30 g of the polymer was obtained by drying the polymer collected here under reduced pressure.

5       The determination of the structure of the obtained polymer was performed by  $^1\text{H}$ -NMR (FT-NMR: Bruker DPX400; resonant frequency: 400 MHz; nuclide measured:  $^1\text{H}$ ; solvent used: d-DMSO; measurement temperature: room temperature). The results of  $^1\text{H}$ -  
10 NMR showed a peak resulted from methyl sulfonate at 3 to 4 ppm and accordingly it was confirmed that the obtained polymer was a polyhydroxyalkanoate containing a unit represented by the following chemical formula (64) as a monomer unit.

15       [0336]

[chemical formula 100]



[0337]

As for the ratio of the units in the  
20 polyhydroxyalkanoate represented by the chemical

formula (64), it was confirmed that it was a copolymer having a monomer ratio of 8 mol% for unit G and 92 mol% for unit H.

[0338]

5        In addition, there was no peak observed resulted from sulfonic acid in acid value titration using Potentiometric Titrator AT510 (product of Kyoto Electronics Manufacturing Co., Ltd.) and it was also made evident from this that sulfonic acid was  
10 converted to methyl sulfonate.

[0339]

The average molecular weight of the obtained polymer was estimated by gel permeation chromatography (GPC; TOSOH, column; Polymer 15 Laboratories PLgel 5  $\mu$  MIXED-C, solvent; DMF/LiBr 0.1% (w/v), polystyrene conversion). Consequently, the number average molecular weight, Mn was 15,900, and weight average molecular weight, Mw was 24,200.

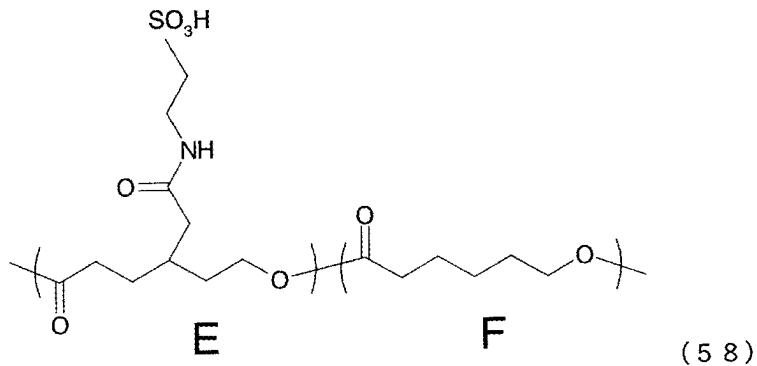
[0340]

20 (Example 31)

Esterification reaction of the polyhydroxyalkanoate which consists of a unit represented by chemical formula (58) synthesized in Example 24

25 [0341]

[chemical formula 101]



[0342]

0.30 g of the polyhydroxyalkanoate copolymer which consists of a unit represented by the chemical formula (58) (E: 12 mol%, F: 88 mol%) obtained in Example 24 was added to an eggplant flask and dissolved with 21.0 ml of chloroform and 7.0 ml of methanol added and cooled to 0°C. 1.34 ml of 2 mol/L trimethylsilyldiazomethane-hexane solution (product of Aldrich) was added to this, and agitated for 4 hours. After the reaction ended, the solvent was removed with an evaporator and the polymer was collected.

[0343]

21.0 ml of chloroform, 7.0 ml of methanol were further added to re-dissolve the polymer and the solvent was removed by an evaporator. This operation was repeated 3 times.

[0344]

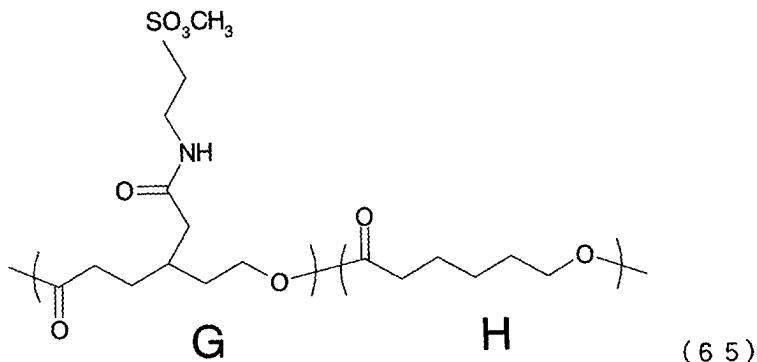
20                0.31 g of the polymer was obtained by drying

the polymer collected here under reduced pressure.

The determination of the structure of the obtained polymer was performed by  $^1\text{H}$ -NMR (FT-NMR: Bruker DPX400; resonant frequency: 400 MHz; nuclide measured:  $^1\text{H}$ ; solvent used: d-DMSO; measurement temperature: room temperature). The results of  $^1\text{H}$ -NMR showed a peak resulted from methyl sulfonate at 3 to 4 ppm and accordingly it was confirmed that the obtained polymer was a polyhydroxyalkanoate containing a unit represented by the following chemical formula (65) as a monomer unit.

[0345]

[chemical formula 102]



15 [0346]

As for the ratio of the units in the polyhydroxyalkanoate represented by the chemical formula (65), it was confirmed that it was a copolymer having a monomer ratio of 12 mol% for unit 20 G and 88 mol% for unit H.

[0347]

In addition, there was no peak observed resulted from sulfonic acid in acid value titration using Potentiometric Titrator AT510 (product of Kyoto Electronics Manufacturing Co., Ltd.) and it was also made evident from this that sulfonic acid was converted to methyl sulfonate.

[0348]

The average molecular weight of the obtained polymer was estimated by gel permeation chromatography (GPC; TOSOH, column; Polymer Laboratories PLgel 5  $\mu$  MIXED-C, solvent; DMF/LiBr 0.1% (w/v), polystyrene conversion). Consequently, the number average molecular weight, Mn was 14,700, and weight average molecular weight, Mw was 21,800.

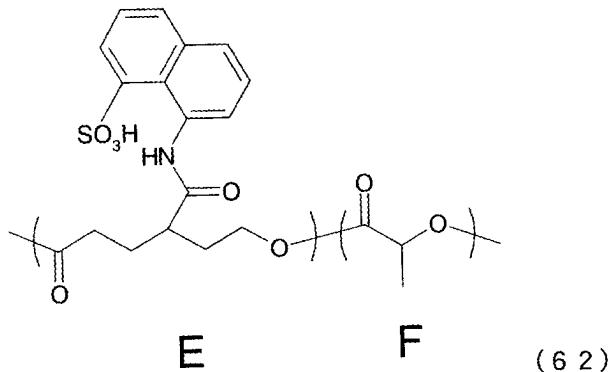
[0349]

(Example 32)

Esterification reaction of the polyhydroxyalkanoate which consists of a unit represented by chemical formula (62) synthesized in Example 28

[0350]

[chemical formula 103]



[0351]

0.30 g of the polyhydroxyalkanoate copolymer which consists of a unit represented by the chemical 5 formula (62) (E: 8 mol%, F: 92 mol%) obtained in Example 28 was added to an eggplant flask and dissolved with 21.0 ml of chloroform and 7.0 ml of methanol added and cooled to 0°C. 1.34 ml of 2 mol/L trimethylsilyldiazomethane-hexane solution (product 10 of Aldrich) was added to this, and agitated for 4 hours. After the reaction ended, the solvent was removed with an evaporator and the polymer was collected.

[0352]

15 21.0 ml of chloroform, 7.0 ml of methanol were further added to re-dissolve the polymer and the solvent was removed by an evaporator. This operation was repeated 3 times.

[0353]

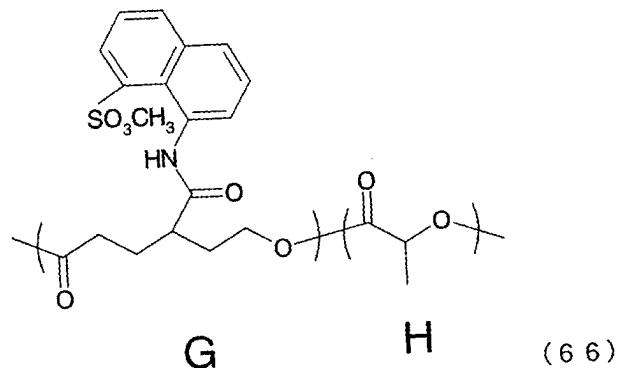
20 0.30 g of the polymer was obtained by drying

the polymer collected here under reduced pressure.

The determination of the structure of the obtained polymer was performed by  $^1\text{H}$ -NMR (FT-NMR: Bruker DPX400; resonant frequency: 400 MHz; nuclide measured:  $^1\text{H}$ ; solvent used: d-DMSO; measurement temperature: room temperature). The results of  $^1\text{H}$ -NMR showed a peak resulted from methyl sulfonate at 3 to 4 ppm and accordingly it was confirmed that the obtained polymer was a polyhydroxyalkanoate containing a unit represented by the following chemical formula (66) as a monomer unit.

[0354]

[chemical formula 104]



15 [0355]

As for the ratio of the units in the polyhydroxyalkanoate represented by the chemical formula (66), it was confirmed that it was a copolymer having a monomer ratio of 8 mol% for unit G and 92 mol% for unit H.

[0356]

In addition, there was no peak observed resulted from sulfonic acid in acid value titration using Potentiometric Titrator AT510 (product of Kyoto Electronics Manufacturing Co., Ltd.) and it was also made evident from this that sulfonic acid was converted to methyl sulfonate.

[0357]

The average molecular weight of the obtained polymer was estimated by gel permeation chromatography (GPC; TOSOH, column; Polymer Laboratories PLgel 5  $\mu$  MIXED-C, solvent; DMF/LiBr 0.1% (w/v), polystyrene conversion). Consequently, the number average molecular weight, Mn was 7,500, and weight average molecular weight, Mw was 11,400.

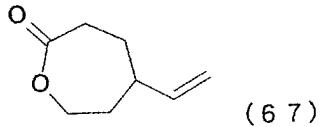
[0358]

(Example 33)

(Synthesis of polyester using 5-ethenyl-2-oxepanone represented by chemical formula (67) and  $\epsilon$ -caprolactone)

[0359]

[chemical formula 105]



[0360]

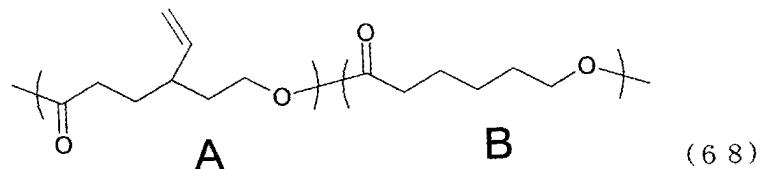
0.31 g (2.0 mmol) of 5-ethenyl-2-oxepanone represented by the chemical formula (67), 1.14 g (10.0 mmol) of  $\epsilon$ -caprolactone, 4.8 ml of 0.01 M toluene solution of tin octylate (tin 2-5 ethylhexanoate), 4.8 ml of 0.01 M toluene solution of p-tert-butylbenzyl alcohol were placed in a polymerization ampoule and after performing drying under reduced pressure for 1 hour and nitrogen purge, it was heat-sealed under reduced pressure, and heated 10 at 150°C to perform ring-opening polymerization. The reaction was ended after 12 hours and the reaction product was cooled. The obtained polymer was dissolved in chloroform and re-precipitated in methanol in an amount of 10 times of the chloroform 15 required for dissolving the polymer. The precipitation was collected and 0.86 g of polymer was obtained by carrying out drying under reduced pressure.

[0361]  
20 In order to identify the structure of the obtained polymer, NMR analysis was performed on the same conditions as in Example 1 and consequently it was confirmed that the obtained compound was a polyhydroxyalkanoate copolymer which contains a unit 25 represented by the following chemical formula (68) as a monomer unit. It was also confirmed that the ratios of monomer units were 12 mol% for A unit and

88 mol% for B unit.

[0362]

[chemical formula 106]



5 [0363]

The average molecular weight of the obtained polyhydroxyalkanoate was estimated by gel permeation chromatography (GPC; TOSOH HLC-8220, column; TOSOH TSK-GEL Super HM-H, solvent; chloroform, polystyrene conversion). Consequently, the number average molecular weight, Mn was 17,500, and weight average molecular weight, Mw was 25,400.

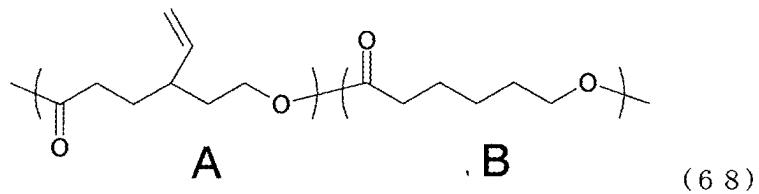
[0364]

(Example 34)

15                 Oxidation reaction of polyhydroxyalkanoate which consists of a unit represented by chemical formula (68) synthesized in Example 33

[0365]

[chemical formula 107]



[0366]

0.50 g of a polyhydroxyalkanoate copolymer which consists of a unit represented by the chemical formula (68) (A: 12 mol%, B: 88 mol%) obtained in Example 33 was added to an eggplant flask and dissolved with 30 ml of acetone added. This was placed in an ice bath, and 5 ml of acetic acid and 0.40 g of 18-crown-6-ether were added and the mixture was agitated. Next, 0.32 g of potassium permanganate was slowly added on the ice bath, and agitated in an ice bath for 2 hours, and agitated at room temperature for further 18 hours. 60 ml of ethyl acetate was added after the reaction ended, and 45 ml of water was further added. Next, sodium hydrogen sulfite was added until peracid was removed. Then, the pH of the liquid was adjusted to 1 with 1.0 N hydrochloric acid. The organic layer was extracted and washed 3 times with 1.0 N hydrochloric acid. After the organic layer was collected, crude polymer was collected by evaporating the solvent. Next, polymer was collected, after washed with 50 ml of water, 50 ml of methanol and further with 50 ml of

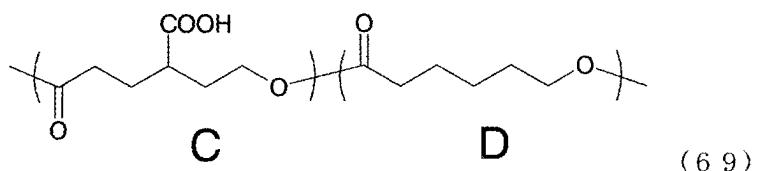
water 3 times. Next, it was dissolved in 3 ml of THF, re-precipitation was performed using methanol in an amount of 50 times of THF required for dissolving the polymer. The precipitation was collected and 0.42 g 5 of polymer was obtained by carrying out drying under reduced pressure.

[0367]

In order to identify the structure of the obtained polymer, NMR analysis was performed on the 10 same conditions as in Example 1 and consequently it was confirmed that the obtained compound was a polyhydroxyalkanoate which contains a unit represented by the following chemical formula (69) as a monomer unit.

15 [0368]

[chemical formula 108]



[0369]

The average molecular weight of the obtained 20 polyhydroxyalkanoate was estimated by gel permeation chromatography (GPC; TOSOH HLC-8220, column; TOSOH TSK-GEL Super HM-H, solvent; chloroform, polystyrene conversion). Consequently, the number average

molecular weight, Mn was 14,300, and weight average molecular weight, Mw was 21,500.

[0370]

In order to calculate the unit of the obtained  
5 polyhydroxyalkanoate furthermore, carboxyl groups at  
the end of the side chains of the  
polyhydroxyalkanoate were subjected to methyl  
esterification using trimethylsilyldiazomethane and  
the calculation was performed.

10 [0371]

30 mg of the target polyhydroxyalkanoate was  
added to 100 ml-volume eggplant flask and dissolved  
with 2.1 ml of chloroform and 0.7 ml of methanol  
added. 0.5 ml of 2 mol/L trimethylsilyldiazomethane-  
15 hexane solution was added to this, and agitated at  
room temperature for 1 hour. After the reaction  
ended, the solvent was removed and the polymer was  
collected. It was washed with 50 ml of methanol and  
the polymer was collected after that. 29 mg of  
20 polyhydroxyalkanoate was obtained by carrying out  
drying under reduced pressure.

[0372]

NMR analysis was performed on the same  
conditions as in Example 1 and consequently it was  
25 confirmed that the obtained polyhydroxyalkanoate  
represented by the chemical formula (69) was a  
copolymer having a monomer ratio of 11 mol% for C

unit and 89 mol% for D unit.

[Industrial Applicability]

[0373]

A novel polyhydroxyalkanoate which contains a  
5 vinyl group, which is a reactive group, on a side  
chain in a molecule, a novel polyhydroxyalkanoate  
which contains a carboxyl group in a molecule, a  
novel polyhydroxyalkanoate which contains a unit  
having an amide group and a sulfonic acid group in a  
10 molecule, and a production method thereof are  
provided by the present invention. These new  
polyhydroxyalkanoates having a vinyl group or a  
carboxyl group can have functional groups introduced  
therein utilizing these reactive groups, and  
15 accordingly can be applied to functional materials.  
Furthermore, polyhydroxyalkanoates which contain in a  
molecule a carboxyl group and a unit having an amide  
group and a sulfonic acid group are excellent in melt  
processability, and also excellent in  
20 biocompatibility due to their hydrophilicity, and can  
be expected to be applied to soft materials for  
medical use, etc.

[Document] ABSTRACT

[Abstract]

[Problem to be solved] To provide a novel polyhydroxyalkanoate having a reactive functional group in a molecule, and a production method thereof,  
5 etc.

[Solution] By utilizing the vinyl group of polyhydroxyalkanoate which contains a unit having a vinyl group on a side chain, a polyhydroxyalkanoate  
10 which contains a carboxyl group and a unit having an amide group and a sulfonic acid group in a molecule is derived.

[Elected drawing] None